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of
Synthetic Substances

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By Dr. Emil Dreher

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Translated by
MARION LEE TAYLOR

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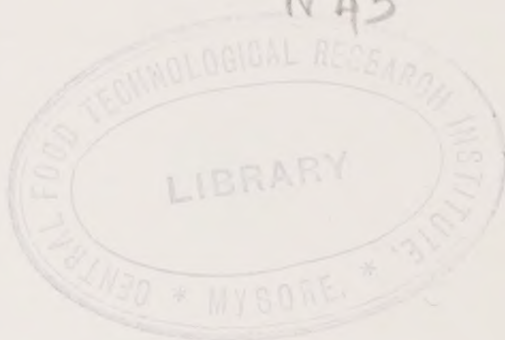
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THE CHEMISTRY OF SYNTHETIC SUBSTANCES

CONTENTS

INTRODUCTION

The chemistry of macromolecular organic compounds, rapidly developed in science and industry, has up to now been considered in existing literature chiefly in the realm of technical application, especially in so far as it concerns the treatment of high molecular substances. By the synthesis of diverse macromolecular compounds of which the synthetic substances so desired today consist, the range of problems of organic chemistry has been essentially extended, while the latter has at the beginning been unable to keep pace in the solution of the underlying theoretical questions. Therefore it is not without significance that the Organic Chemist has been able in recent years, along with the previous patent literature merely describing technical processes, to make use of a comprehensive work: "The High Molecular Organic Compounds", in which for the first time the requirements applicable to the synthesis and structure of macromolecular organic, natural and synthetic compounds were determined by scientific experiments. Besides the treatment of the theoretical questions of interest, as for example, of the physical qualities adhering to high molecular substances, sometimes by the decided physical chemical method of work, nevertheless organic chemistry has remained of decisive significance for the synthesis and research of synthetic high moleculars. The consideration of these natural, unchanged or chemically changed products, as particularly the numerous synthetic high moleculars, from the point of view of their applicability to low molecular organic substances often make possible a just as unequivocal estimate and standard of value. Such knowledge is undoubtedly beneficial for synthesis and decisions of technical application. Absorption in such fundamental, organic-chemical questions is therefore indispensable for the expert in the production and manufacture of synthetic substances, and will be of great value to the student. Especially for the latter such representations bring a certain completion of knowledge in the great realm of organic chemistry, for the organic textbooks heretofore produced still give very slight consideration to this latest and very important branch of organic chemistry.

Such reasons and numerous letters from groups interested in high molecular chemistry made the pub-

lishers decide to bring out a collection of essays previously published. Along with other more recent works of value in the field of the chemistry of synthetic substances, of caoutchouc, cellulose, and paint media, the present collection is justified if it can assist in giving a survey of the principal questions of macromolecular chemistry and if, consequently, it can be of aid to practice. It lays no claim to be regarded as a scientific work but as an introduction to acquaintance with the chemical processes taking place in the production of synthetic substances.

Ludwigshafen am Rhein.

The Author.

HIGH MOLECULAR ORGANIC COMPOUNDS
Determination of Molecular Weight

by Measurement of Viscosity[1])

The chemistry of high molecular organic compounds has experienced for some years an enormous technical rise. We shall only refer briefly here to the growing production of artificial silk, synthetic caoutchouc, artificial resins, and synthetic substances chiefly in Germany and America.

In this connection scientific research has smoothed the way considerably for industrial chemistry. The views of H. Staudinger concerning the structure of high molecular compounds were highly successful and are being confirmed more and more. The development extends to the technical preparation as well as especially to the production of synthetic organic molecular compounds.

Even without need of devices and scarcity of raw materials countries like America and England work methodically towards the production of synthetic high molecular compounds. Since scientfic knowledge and methods of work have penetrated this branch of organic-technical chemistry great results have not been lacking. A deepening and generalisation of these relationships will also be of further advantage. Even today the young chemist and engineer should more than ever before make acquaintance at the university with this branch of organic chemistry; for the chemistry of high molecular compounds has taken its place by the side of that of low molecular compounds. The total picture of the modern chemistry of organic high molecular substances can be closely connected with that of colloid chemistry. Here and there we have chemical compounds which by their size and shape have peculiar properties of a chemical and physical nature. As a new branch of organic chemistry these organic high molecular compounds present a very great number of peculiarities, great variety, and an almost inexhaustible applicability. Their development shows that these high molecular organic compounds or organic colloids no longer belong "to the world of neglected dimensions".

The high molecular organic molecules are not composed of a few hundred atoms like the low moleculars, but of many thousand atoms. High molecular substances can be produced either by polymerisation or by polycondensation or perhaps even by the combination of

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these two properties in the same molecule[2]). The molecules may be homoeopolar or heteropolar. The form of the molecules is here of far greater decisive significance than in the case of the low molecular compounds. For by far the greater number of these high molecular molecules the two-dimensional or threadlike form is characteristic (linear colloids according to Staudinger). Other macromolecules have three-dimensional or spherical form (sphero-colloids). By the term macromolecule Staudinger understands a molecule in which at least thousands of atoms are combined by main valences and moreover in one or several dimensions[3]). The special properties of these threadlike or spherical mass-molecules, as said, play a great part in technology; for example, firmness, toughness, elasticity, capacity for forming resin or fibers are in close connection with the special form of these molecules. The viscosity of the solutions of high molecular compounds is an important characteristic. Thus it is shown that low molecular compounds give solutions of **low viscosity** even when the solutions are concentrated. **Threadlike** high molecular compounds on the other hand yield according to the length of their molecules **highly viscous** solutions even when slightly concentrated. Macromolecules of **spherical** form in a concentrated solution yield only solutions of **low viscosity.**

Precisely this quality of the high molecular molecules has been drawn upon by Staudinger for the determination of their constitution, in order by this means to penetrate the copious abundance of the organic high molecular world. Hence today very definite statements can be made regarding the structure of high molecular natural and synthetic molecules. By this means it has been made possible for technology to undertake in a very simple manner a test of these natural and also synthetic substances in definite directions. Important branches of industry, for example, the cellulose-artificial silk industry and that of the synthetic substances have already been able to make effective practical use of these views regarding the structure of cellulose, caoutchouc, and of many synthetic high polymeric compounds. How important these relationships may be for technology follows from the fact that the physical properties are in very definite relationship with the increasing molecular mass of these organic, natural or synthetic substances; for on their molecular mass, depends their solubility, the colloid nature of the solutions, the toughness,

elasticity, tensile strength, hardness, steadiness of cold or heat, and, as said, capacity for forming resin and film. Therefore it is in many ways of extraordinary significance for technology to obtain information regarding the structure of definite high molecular substances, that is, also regarding the degree of polymerisation. Other relationships and manifestations can then be explained with far greater ease and lucidity. Thereby a choice of substances and their demarcations can also be attained. Let us mention here only the production of polyvinyl acetate. From the great number of polymerisates of vinyl acetate that can be produced only a comparatively small number with the definite properties desired, such as sufficient adhesive capacity, liquescence, capacity of combining splinters, and many others, are suited to the production of intermediate strata with flexing and expanding elasticity. In this the degree of polymerisation actually plays a great part in the choice of products. But simultaneously with the determination of viscosity an analysis of an organic high molecular molecule can be carried on, for example, the analysis of cuprammonium rayon in Schweizer's solution by the action of oxygen. These examples might be extended to very many synthetic soluble polymeres and products of polycondensation. But in many cases instead of determining the degree of polymerisation it is sufficient to follow the course of a condensation or polymerisation reaction by measuring the viscosity in order to interrupt it at a given time. The use of this method has long been known to technology and is employed for example in the varnish industry in the polymerisation of oil and also in the reaction of polyesterifiication.

In the following closer consideration and principles of determination of molecular mass or degree of polymerisation are to be demonstrated briefly[4]). It might therefore be of interest to those closely connected with this periodical to know how the difficulties are overcome opposing the clarification of the constitution of the high polymeric compounds and the determination of their molecular weights. Especially the execution of measurement of viscosity according to **Staudinger** is explained here in broad strokes in order possibly to make allusion to it at various points.

DETERMINATION OF THE MOLECULAR WEIGHT

The application of measurement of viscosity for determination of molecular weight is possible only in the
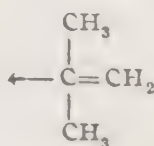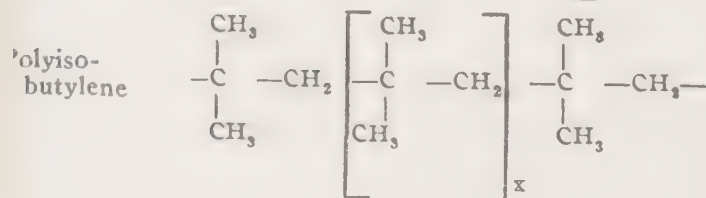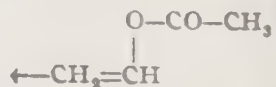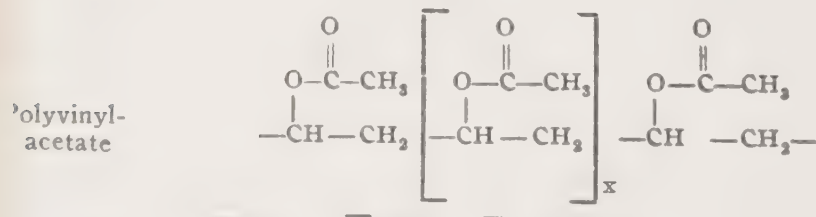
case of **soluble** macromolecules, which, having two-dimensional structure, may therefore pass for thread-formed molecules.

It is known from Staudinger's works that the hypothesis has been realized practically in an exceedingly large number of high moleculars formed by polymerisation. In such polymeric molecules the true chain-forming molecule groups are preserved. The chain-shaped or

TABLE I

	Polymerisation-molecules	Monomeric molecules
Polystyrol	$-\overset{C_6H_5}{\underset{}{CH}}-CH_2 \left[-\overset{C_6H_5}{\underset{}{CH}}-CH_2- \right]_x \overset{C_6H_5}{\underset{}{CH}}-CH_2-$	$\leftarrow -\overset{C_6H_5}{\underset{}{CH}}=CH_2$
Caoutchouc	$-CH_2-\overset{CH_3}{\underset{}{C}}=CH-CH_2 \left[-CH_2-\overset{CH_3}{\underset{}{C}}=CH-CH_2 \right]_x -CH_2-\overset{CH_3}{\underset{}{C}}= [\overset{}{CH_2-CH}$	$\leftarrow -CH_2-\overset{CH_3}{\underset{}{C}}-CH=CH_2$
Polypropenyl benzene	$-\overset{C_6H_5}{\underset{}{CH}}-CH_3-CH_2 \left[-\overset{C_6H_5}{\underset{}{CH}}-CH_3-CH_2 \right]_x -\overset{C_6H_5}{\underset{}{CH}}-CH_2-CH_2-$	$\leftarrow -\overset{C_6H_5}{\underset{}{CH}}=CH-CH_3$
Polyacrylic acid	$-\overset{COOH}{\underset{}{CH}}-CH_2 \left[-\overset{COOH}{\underset{}{CH}}-CH_2 \right]_x -\overset{COOH}{\underset{}{CH}}-CH_2-$	$\leftarrow -\overset{COOH}{\underset{}{CH}}=CH_2$
Polyoxy-methylene	$-CH_2-O- \left[CH_2-O \right]_x -CH_2-O-CH_2-O-$	$\leftarrow -CH_2=O$
Polyvinyl-acetate	$-\overset{O-\overset{\overset{O}{\|\|}}{C}-CH_3}{\underset{}{CH}}-CH_2 \left[-\overset{O-\overset{\overset{O}{\|\|}}{C}-CH_3}{\underset{}{CH}}-CH_2 \right]_x -\overset{O-\overset{\overset{O}{\|\|}}{C}-CH_3}{\underset{}{CH}} -CH_2-$	$\leftarrow -\overset{O-CO-CH_3}{\underset{}{CH}}=CH_2$
Polyiso-butylene	$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2 \left[-\overset{CH_3}{\underset{CH_3}{C}}-CH_2 \right]_x -\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$	$\leftarrow -\overset{CH_3}{\underset{CH_3}{C}}=CH_2$

threadlike molecules occur in this way that by compensation of valence in the case in question after previous migration of hydrogen atoms, the double compounds originally present disappear and clear the way for a chain. Along with the the monomeric molecules are mostly transformed after a slow but strong activation in the rapid course of a chain-reaction into high molecular molecules generally of two dimensions. (See Table I).

The usual method of determining size of molecules, for example, osmotic pressure, cryoscopy, have thus far failed in the case of these substances because of the size of the molecules. This does not only hold true for a high molecular polystyrol with a molecular weight of about 600000, but is true also for cellulose, cellulose acetate, cellulose ether, caoutchouc, ordinary polystyrols, polyindenes, polyacrylic acid, and a very considerable number of other products of polymerisation and polymerisates of importance to technology as synthetic substances and basic materials of lacquers[5]). Most recently however it has become possible to determine molecular weight in high molecular compounds by osmosis and the **Svedberg** method of ultracentrifuge[6]). But these methods are not as simple, rapid and cheap as the measurement of viscosity.

Further the attempt has been made to employ measurement of viscosity also for the determination of molecular weight in soluble high molecular compounds which have not been formed by **polymerisation** but by **polycondensation.** To polycondensations belong, as is known, reactions in which macromolecules are formed from small molecules by efflux of water or ammonia, which may be chain-shaped or even three-dimensional. For example, the condensation of p-cresol and formaldehyde in a corresponding manner of reaction yields two-dimensional molecules[7]) while the reaction of phenol or meta-cresol or urea with formaldehyde can form besides threadlike macromolecules also reticulated spherical macromolecules. In the case of para-cresol resins a reticulation of molecules is not easily possible, as the para position still reactive in phenol is already occupied. Likewise chain-formed polycondensates are produced in the condensation of polybasic acids with polyalcohols[8]). (Cf. Table II). The most interesting of these high molecular products of polycondensation especially with regard to manifestations of viscosity in connection with their structure are: phenol-formaldehyde—condensation-products [9] -phenol-urea-condensation-products [10] -alkyd-

TABLE II

Polycondensation Molecules		Momomeric Molecules
Para-cresol-formaldehyde products of condensation	(structural formula of para-cresol-formaldehyde polycondensate: benzene rings with OH, CH_3, CH_2 groups)	$\longrightarrow -H_2O$ (para-cresol ring with OH, CH_3) $+ H_2CO$
Urea-Formaldehyde products of condensation	(structural formula with $-CH_2-N-C-N-CH_2$, $O=C$, CH_2, N chains)	$\xrightarrow{-H_2O} \;\; H_2N-CO-NH_2$ $+ H_2CO$
Poly-succinic-acid-glycol-ester	$-CH_2-CH_2-O-\left[-\overset{O}{\underset{\|}{C}}-CH_2-CH_2-\overset{O}{\underset{\|}{C}}-O-CH_2-CH_3\right.$ ... $\left.-O-\overset{O}{\underset{\|}{C}}-CH_2-CH_2-\overset{O}{\underset{\|}{C}}-O-\right]_x$	$\xleftarrow{-H_2O}$ $HOOC-CH_2-CH_2-COOH$ $+ HO-CH_2-CH_2-OH$

resins[11]—various film-forming substances connected with the production of varnish[11]a). It has also been known in the case of pectin substances that they manifest quite similar relationships as cellulose for example. Next to the possible clarification of constitution, the measurement of viscosity is a gauge for the high molecular character and capacity for coagulation of these natural products[12]).

Since it has been shown that the dissolved colloid particles of the very great majority of high molecular compounds show threadlike or chain-formed macromolecules, the determination of the size of the particles yields simultaneously their molecular weight. (By molecular weight is to be understood average molecular weight). The former usual methods, such as the cryoscopic and osmotic, have, as stated, a very limited field of application. Thus by the cryoscopic methods are determined molecular weights only as high as about 10000 at most. But opposed to that however one can proceed with the determination of molecular weight by measuring the viscosity not only exercising empiric control, but the size of the molecules can also be determined with fair accuracy, both of the low molecular as of the highest molecular representatives.

The method was first tested with paraffin hydrocarbon substances with hydrocarbon chains of different lengths and further with synthetic high molecular compounds of threadlike form. It was shown that only the true carbon chain exercises an influence on viscosity while side groups are of but secondary significance. The composition of all these products can be affected without difficulty, and the process of polymerisation can for the most part be considerably influenced by changing the conditions of the reaction (temperature, catalyser, dilution). Thus there arise products of varying high molecular weight and, as already mentioned, of diverse physical properties. Thus the constitution of many of these high molecular products of polymerisation and of polycondensation have been made clear. (Tables I and II show some examples).

By studying the viscosity of diluted solutions of threadlike high molecular compounds, a connection was established between viscosity and molecular weight, this connection being illustrated by the following formula:

$$\frac{\eta sp}{c} = K_m. M \qquad 1)$$

from which

$$M = \frac{\eta sp}{c . K_m} \qquad 2)$$

in which η sp = specific viscosity; c = fundamental molarity; M = molecular weight; K_m = a characteristic constant for every kind of substance. The specific viscosity is derived from the relative viscosity according to the formula:

$$\eta r - 1 = \eta sp \qquad 3)$$

The relative viscosity is obtained by dividing the time of efflux of solution by that of the solvent.

$$\eta r = \frac{(time) \ solution}{(time) \ solvent}$$

η sp then represents the increase of viscosity produced by the dissolved substance. The measurement of viscosity itself is carried out in the **Ostwald** viscosimeter at a constant temperature of 200° in thermostats[13]). For the technical performance of viscosity measurement the following data may suffice:

PROCESS OF DETERMINING VISCOSITY

The substance to be measured is dissolved properly concentrated in a ccm measuring flask; a part of this solution is filtered through a glass filter without loss of solvent. 3ccm of this are then charged into a clean, dry viscosimeter. The upper bulb of the viscosimeter has a volume of 1ccm, and the lower bulb a volume of 10 ccm. The capillary vessel is approximately 10 ccm long. The capillary capacity is so to be chosen that the duration of flow of the solvent used amounts to about 120-200 seconds. The time of flow of the solution should be at least 10 seconds longer than that of the solvent. An exact stopwatch is important. The viscosimeter is installed in a thermostat. The solution in the viscosimeter is put under high pressure at the time of measurement by dry air or in the case of substances sensitive to oxygen by nitrogen. In the case of substances sensitive to oxygen, as for ex. cellulose, the conversion of the solution and the measurement must take place in an atmosphere of nitrogen. At the time approximately 3-5 measurements are made and the mean of the time of efflux employed. The solvent must be measured in the same viscosimeter.

The equation 1) above is only valid when working in the field of diluted solutions, so that the molecules do

not interfere mutually. By c the basic-molarity is denoted, that is, the concentration with which a basic molecule is dissolved in a litre of the solvent.

In the case of normal paraffins having the basic molecule methylene, $-CH_2-$ = 14, a basic molar solution therefore contains C = 1, = 14 gr. paraffin, no matter what chain-length or what degree of polymerisation of the solvent in the litre.

In the case of styrol, for ex., a basic molar solution contains correspondingly 104 gr. per litre, in the case of propenylbenzol = 118 gr.: in the case of cellulose = 162 gr.; in the case of polyisobutylene 56 gr.; etc.

Therefore knowledge of the basic molecule is required from which the high polymeric compound originated. The number of repetitions of the basic molecule in the high polymeric macromolecule gives its degree of polymerisation.

Degree of polymeris. =
$$\frac{\text{mol. wt. of polymer. molec.}}{\text{mol. wt. of monomer. molecular molec.}}$$

(By degree of polymerisation is meant the average degree of polymerisation). By knowing the K_m-constant of a certain species of substance, the time of viscosity or efflux therefore, the molecular weight of the substance in question can be calculated (according to formula 2).

The K_m constants given in the fololwing Table III selected for various species of substances were actually determined in comparison with definite compounds. They possess a satisfactory degree of exactness for technical experimental purposes. The agreement of the K_m-constants obtained in low molecular hydrocarbons or even products of polymerisation with those found in high moleculars furnishes clear proof that these large molecules have the same extended threadlike formation as the small particles.

In performing the measurement of viscosity it is naturally to be noted that the high polymeric compounds are divided into easily dissolving solvents or those easily converted into a sol in low concentration. The top limit for specific viscosity is approximately η sp = 0.02 — 0.2. Correspondingly the measurements of viscosity must be carried out in low concentration as basic molar, for ex., 0.1 or 0.01 basic molar.

TABLE III

K_m—Constants for Polymeric Compounds[14])

Substance	Basic Molecule	$c = 1$ 1 gr. basic molecule solut. per litre of solvent	Solvent	K_m-Constants combined partly with regard to different solvents
Paraffins	CH_2	14	Benzol, Tetralin, Toluol	1.3×10—4
Polyprenes (caout-chouc, balata)	C_5H_8	68	,,	3.0×10—4
Polypranes	C_5H_{10}	70	,,	3.0×10—4
Polyisobutylenes	C_4H_8	56	,,	1.75×10—4
Polystyrols	C_8H_8	104	,,	1.8×10—4
Polyindenes	C_9H_8	116	,,	1.8×10—4
Polypropenyl benzols and derivatives	C_9H_{10}	118	,,	2.9×10—4
Polyethylene oxides	C_2H_4O	44	,,	1.8×10—4
Polyacrylacids	$C_3H_4O_2$	72	2nNaOH	2.1×10—4
(Acryl derivatives vinyl derivatives)	corresponding corresponding	corresponding	acetic ether acetone	1.8×10—4
Cellulose	$C_6H_{10}O_5$	162	Cupric-oxide-ammonia ..	5.0×10—4
Ntrocellulose[7])	C_6H_7 $0_{11}N_3$	298	acetone amylacetate	11.0×10—4
Cellulose Acetate[7])	$C_{12}H_{16}0_8$	288	Acetone	11.0×10—4
(Ethyl cellulose)			Chloroform	11.0×10—4
(Methyl cellulose)			Chloroform	11.0×10—4

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[2]) For ex. the reaction of oxystyrol with formaldehyde. Unpublished experiment of the author.

[3]) Cf. H. Staudinger: Angew. Chemie (Applied Chemistry) 49. 801 (1936).

[4]) Cf. E. Dreher: Farbe und Lack (Paint and Varnish) (1935), 483.

[5]) Cf. F. Ohl, Farbe und Lack, 17, 195 (1935).

[6]) G. V. Schulz, Angew. Chemie 49, 549 (1936); also 49, 863 (1936).

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cordance with the number of the chain-equation could be deter-
mined.

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SURVEY OF RELATIONS OF SYNTHETIC HIGH MOLECULAR COMPOUNDS TO DRYING OILS

An attempt wil lbe made here to present briefly the development of synthetic paint materials[1]). I shall show the views concerning the relations between the formation and structure of high molecular synthetic compounds and the film-formation of drying oils. Especial consideration will be given to synthetic drying oils.

PHYSICAL, FILM-FORMING, HIGH MOLECULAR COMPOUNDS

In the course of recent years, but principally since the end of the war, various synthetic high molecular organic compounds have been successfully produced and applied to various useful purposes. An important province for utilizing many of these products is the technology of paint. The entire development did not spring from the idea of sparing raw materials but of creating refined substances. In part this development has followed the compulsion of the circumstances under consideration. In this connection the introduction of **nitrocellulose** into the production of nitrolac should be borne in mind.

The use of cellulose as the basic material of lac in the form of its **acetyl ester** and **benzyl ester** has been further successfully expanded in the following. Now **chlorocaoutchouc** has also been an important binding agent within this entire development. The **synthetic resin copals** which have become of great importance industrially both in Germany and also a little later in America, further present a clear example of constant effort to produce synthetically a more homogeneous product than nature is able to produce. By this homogeneity of synthetic substances both a more manifold applicability is guaranteed and also special applicability for definite purposes.

Thus in various ways hard resins soluble in oil have been created which in essential properties resemble the fused natural resin copals and are even superior to them by their uniformity, clearness, and solubility. Here belong chiefly the resins obtained from colophony by esterfying with phenol-formaldehyde and glycerin or from colyphony by conversion with maleic acid and glycerin. These resins are therefore based on colophony which has always been of predominant significance in the

lac industry in the form of resin ester and of lime resin.

Increasing interest centers about those resins derived from phenol, cumarone resin, indene or those formed by conversion of alkyl or aryl substitutent phenols with formaldehyde. These are the so-called **alkylphenol resins** partly soluble in oil.

The **alkyd resins** soluble in oil, present in trade as **alkydals** and **glytals** among others, have then brought decided improvements into the technology of oil lacquer. These resins are obtained by conversion of polybasic acids, principally of phthalic acid or phthalic anhydride, maleic anhydride with univalent or multivalent alcohols and drying or non-drying oils or their sebacic or resinic acids. These alkyd resins are distinguished by their predominant physical properties in contrast to the natural resins and drying oils. Thus their resistance to water and weather, their hardness and elasticity, their durability is of great importance in the production of paints. However useful synthetic substances of remarkable resistance to light have been successfully produced. The reaction between glycerin and phythalic anhydride leads to the formation of a polymeric ester by a polycondensation reaction.
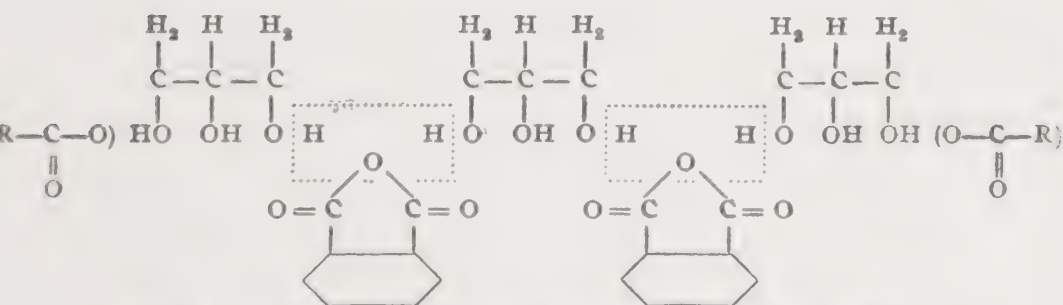
The hydroxyl groups still free here can in sundry ways enter further condensation with new molecules and thus bring about enlargement of the molecule; or they react with drying oils and sebacic acids, for instance eleostearic acid and many others, or resinic acids, for instance abietic acid, with formation of ester and thus give these poly-condensation molecules the character of drying oils. The increase of these molecules can take either a two-dimensional or a three-dimensional direction[2]). This class of resins embraces a great variety of products with diverse physical properties. Thus high molecular resinous products and low molecular substances are known by the type of the drying oils. The resins mentioned at the beginning, which are produced

from colophony by conversion with maleic acid or maleic anhydride and glycerin are further an illustration of the advantageous influence scientific chemistry can have upon industry. Thus the well-known Diels-Alder-Dien synthesis[3]) has here attained important technological significance in the realm of synthetic resins. This interesting reaction has already led to manifold processes. As is known, in the **normal** Dien synthesis an organic molecule with coordinated double bonds

$$-CH_2-CH=CH-CH=CH-CH_2-$$
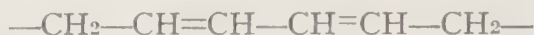
reacts with an organic molecule containing the preferred grouping

$$-\overset{|}{C}=\overset{|}{C}-\overset{O}{\overset{||}{C}}-$$
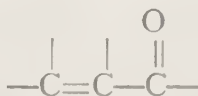
in such a way that the ethylene compounds are dissolved and a union takes place in a 1, 4 arrangement. Thus, for example, a cyclic molecule tetra-hydro-phthalic anhydride, is formed from butadiene and maleic anhydride.
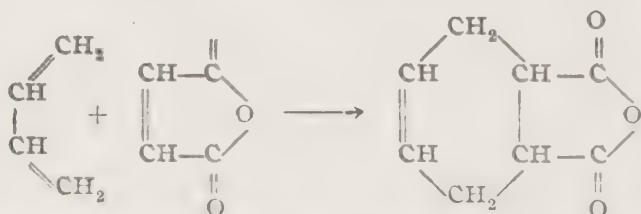
The so-called **abnormal** Dien-synthesis occurs meantime in the reaction of methyl pyrrole and maleic acid. Here a hydrogen atom reacts which by its position is very easily moveable. Here there is no ring formation.
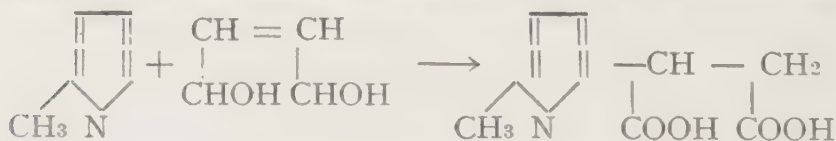
The system of coordinated double bonds occurs not only in the isoprene molecule $CH_2=C-CH=CH_2$ and

$$\overset{|}{CH_3}$$

in butadiene $CH_2=CH-CH=CH_2$, but also in partly hydrogenized benzol derivatives, in higher non-saturated sebacic acids and in other compounds. As examples of non-saturated coordinated acids may be mentioned:

eleostearic acid $CH_3—(CH_2)_3—CH=CH—CH=CH—CH$ $=CH(CH_2)_7—COOH$, which is present in wood oil to about 75%, ketoeleostearic acid (lican acid)

$$CH_3 — (CH_2)_3 — CH = CH—CH = CH—CH = CH$$
$$— (CH_2)_4 — \overset{\displaystyle\|}{\underset{\displaystyle O}{C}} — (CH_2)_2 — COOH$$
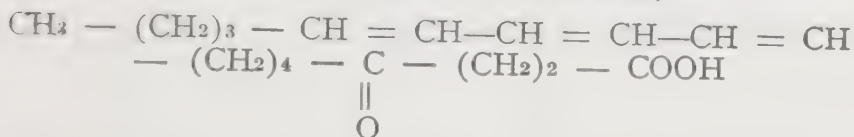
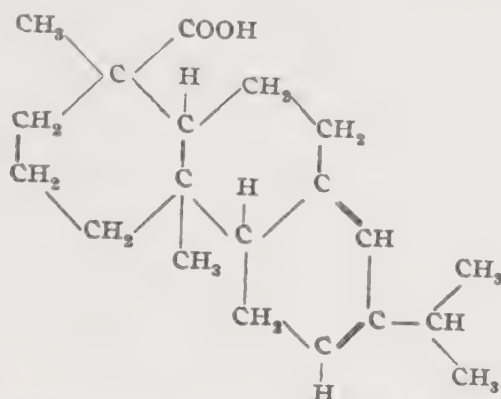in the principal component of oiticica oil[4]), and abietic acid[5]) from colophony

The reactive group $—\overset{|}{C}=\overset{|}{C}—\overset{|}{C}=O$ is found in acrolein $CH_2=CH—\overset{\displaystyle\|}{\underset{\displaystyle O}{CH}}$, in acrylic acid $CH_2=CH—COOH$ as

well as in maleic anhydride respectively in maleic acid.

$$\begin{array}{ccc} CH & = & CH \\ | & & | \\ COOH & & COOH \end{array}$$

Maleic anhydride has become a very important raw material because of its ability to react with diverse original raw materials according to the Dien synthesis. Thus, as already said, resins have been created, produced from abietic acid, colophony, terpenes, and maleic anhydride. By conversion of abietic acid, respectively colophony, with maleic anhydride the following compound is probably formed[6]). (See top of next page).

These first condensation compounds still have free anhydride groups which can react with mono- or polyalcohols under esterification. According to the manner in which the resins are formed, these products are then further treated with drying or non-drying sebacic acids
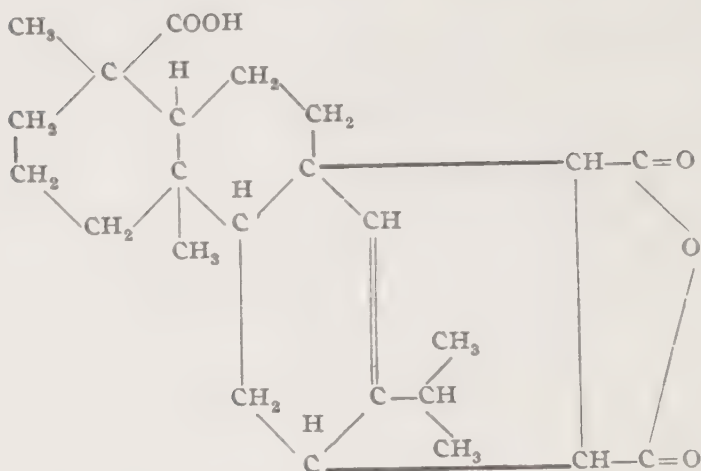
or oils until formation of mixed esters. Reaction pro-
ducts of eleostearic acid (in wood oil) with maleic
anhydride have become known, which have also con-
tributed to the knowledge of wood oils and oiticica
oil[7][8]).
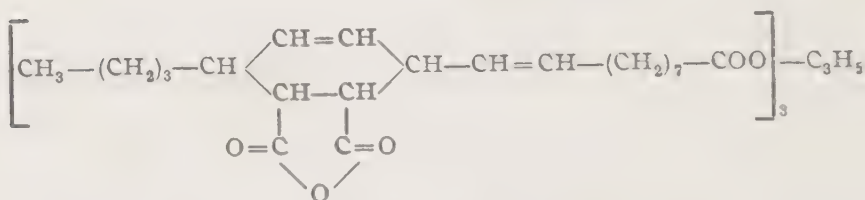
It is worthy of note that the majority of these resins
that have come to prominence in recent years that I have
quoted selectively, are composed of natural products or
at least make the latter necessary for joint employment ;
partly for production, partly for application. These
natural products, such as drying oils, for ex., give these
synthetic high molecular products of polymerisation
and polycondensation[9]) beneficial properties, for exam-
ple, capacity for air-drying, capacity for film forma-
tion, capacity for autocatalytic polymerisation and con-
densation, and conversion of the two-dimensional, linear
molecule structure into three-dimensional, spherical.
These relationships are to be further treated later. Ac-
tually in the case of these compounds it is a question of
partly synthetic products. In this connection mention
should also be made of the processes which have to do
with the conversion of non-drying oils into drying oils.

Schreiber[10]) divides the drying oils into two classes; those with **coordinate** double bonds

$-CH_2-CH=CH-CH=CH-CH_2-$ (wood oil)
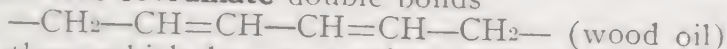
and those which do **not contain coordinate double bonds.**
$-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH$ — (linseed oil and half-drying oils).
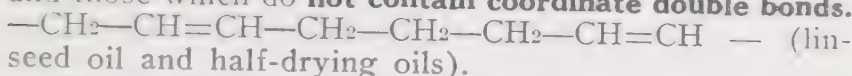
Thus it has become known that the drying process of quick drying oils is to be traced to the presence of coordinate double bonds. Other oils containing only isolated double bonds, can actually be converted into drying oils by the reactions of oxydation (Treatment with air and catalyst at a higher temperature) without any considerable breaking up of the molecule. The CH_2 groups occurring among the double bonds possibly present are thereby oxydized and thus the formation of a coordinate unsaturated system is made possible[11]).

$$-CH = CH-CH_2-CH = CH- \rightarrow -CH = CH-\underset{\underset{O}{\|}}{C}-CH = CH-$$

$$or -CH_2-CH=CH-CH_2-)$$
$$\underset{\underset{OH\ \ OH}{|\ \ \ \ |}}{CH_2-CH-CH-CH_2-} \rightarrow -2H_2O- \rightarrow -CH = CH-CH = CH-$$
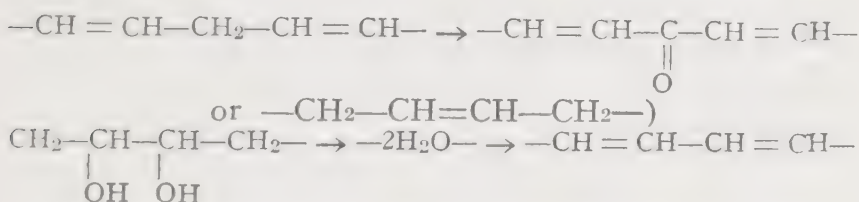
The **purely synthetic high molecular resins** have likewise had a lively development, which have also been important in the technology of paint along with their application as plastic masses. Here first of all it is a question of partly very high molecular products of polymerisation. Only those products shall be mentioned here which are derived from styrol $C_6H_5CH=CH_2$, vinyl chloride $CH_2=CH=Cl$, vinyl alcohol $CH_2=CH-OH$, vinyl acetate, acrylic acid and their derivatives and esters etc. **The self-hardening phenol-formaldehyde-resins** by catalysts at usual temperature will also become of still greater significance.

CHEMICAL FILM-FORMING, HIGH MOLECULAR COMPOUNDS

Examples of natural products forming film by chemical processes are linseed oil and wood oil. But neither here nor abroad have such binding agents been successfully produced by mass technology. To be sure, there have been some partial results. There have been attempts at a solution of the problem by oxydization of hydrocarbons to sebacic acids, which are then converted with

oily hydrocarbons, containing chlorine atoms, hydroxyl groups and non-saturated compounds. Certainly the expectation also persists of obtaining such suitable products from saturated hydrocarbons by the action of carbon monoxide and hydrochloric acid in the presence of aluminium chloride. A similar reaction has been described by Hopff[12]). It has further been proposed to convert polymeric petroleum distillates into suitable products by chlorination and partial extraction of hydrogen chloride, the products later being converted into sebacic acid salts.

A suitable oxydation of coal tar oils and non-saturated products of cracking can also lead to the formation of drying oily compounds[13]). Perhaps even more promising are often deemed those efforts based on acetylene[14]), since acetylene has been successfully converted into polymeric products at normal temperature and with a controllable polymerisation reaction[15]). Such drying oils have already been recently introduced in America under the designation of S.D.O. (Synthetic drying oil). The polymeric derivatives of acetylene, as for ex. vinyl chloride $CH_2=CH-Cl$, vinyl alcohol $CH_2=CH-OH$, etc., have already attained great importance as synthetic substances.

Thus monomeric acetylene, when care is taken for activation by suitable catalysts ($CH\equiv CH- \longrightarrow =C=CH_2$), can react with a second gramme molecule of acetylene and form vinyl acetylene. Two molecules of vinyl acetylene.

$$\overset{\text{Cuprous complex salts}}{CH\equiv CH+=C=CH_2- \rightarrow HC\equiv C-CH=CH_2}$$
$$\text{vinyl acetylene}$$
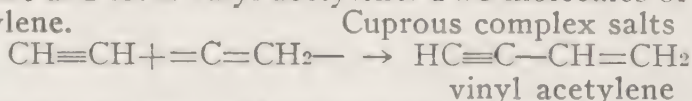
are in the presence of cuprous complex salts united to dimeric acetylene.

$$CH_2=CH-C\equiv CH+=C=CH-CH=CH_2 \rightarrow H_2C=CH$$
$$-C\equiv C-CH=CH-CH=CH_2 \text{ (tetrameric vinyl}$$
acetylene).
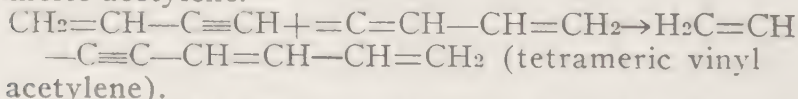
However in the presence of excess acetylene and contacts or by heating (up to 90°) mono-vinyl acetylene reacts to divinyl acetylene[16]). $H_2 = CH-C \equiv CH + = C= CH_2 \rightarrow H_2-CH-C\equiv C-CH=CH_2-CH_2$ (divinyl acetylene). Both mono-and di-vinyl acetylene have in vaporous, fluid, or soluble condition the property of conversion into viscous oils and hard resinous products by means of polymeric catalysts (acid, warmth, pressure) slowly or more quickly according to the conditions of the experiment. The still fluid, but no longer volatile products of polymerisation are pure synthetic, oxydative drying oils of

remarkable permanence in the presence of chemical substances according to the formation of their final state. The process of polymerisation proceeds autocatalytically and leads both to the formation of two-dimensional molecules (Fig. 1a) and surely with the assistance of oxygen to three dimensional molecules (Fig. 1b) (Fig. 1c

Fig. 1.

$$2 \quad HC\equiv C-CH=CH_2 \longrightarrow HC\equiv C-CH-CH-C\equiv CH$$

with underneath CH_2-CH_2

$$+ \left[HC\equiv C-CH=CH_2 \right]_x$$

a)
$$HC\equiv C-CH-CH- \left[\begin{array}{cc} C=CH & CH_2-CH- \\ CH_2-CH- & C=CH \end{array} \right]_x C\equiv CH$$
with CH_2-CH_2

$$HC\equiv C- \left[\begin{array}{c} CH=C- \\ CH-CH_2 \end{array} \right]_x CH-C - CH - CH - C\equiv CH$$
with $-CH-CH_2 \quad CH_2-CH_2$ and O O

b)
$$HC \equiv C - CH - CH - C - CH \left[\begin{array}{cc} CH_2-CH- \\ C - CH \end{array} \right] C\equiv CH$$
with $CH_2-CH_2 \quad CH_2-CH-$ and O O

c)
$$H_2C=CH-C\equiv C-CH-CH_2 \qquad CH_2-CH-C\equiv C-CH=CH_2$$
$$CH_2-CH-C\equiv C-CH-CH_2$$
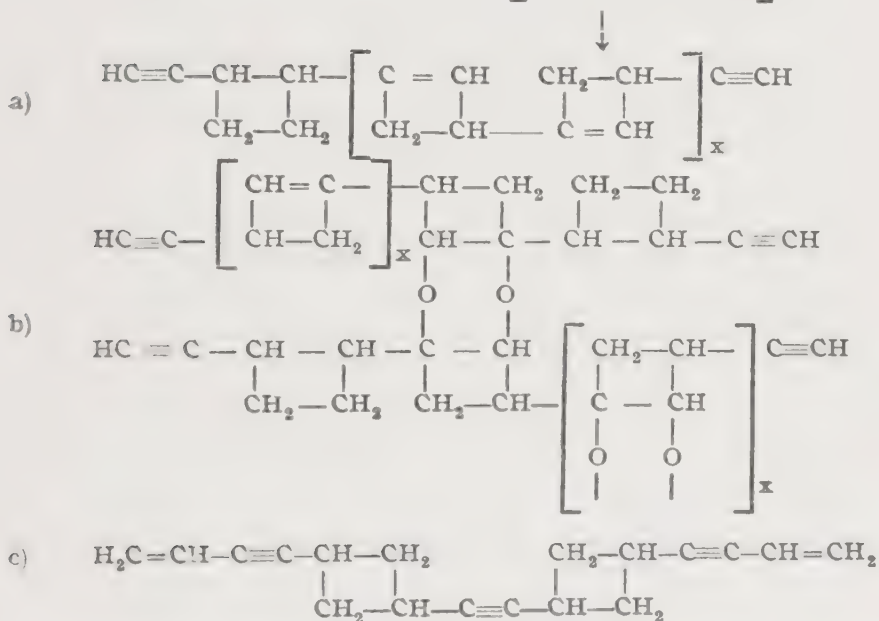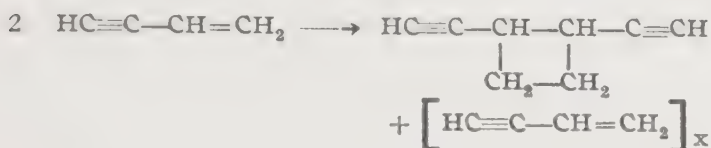
shows a polymeric molecule from divinyl acetylene). The low molecular polymeric products are still soluble in various solvents, react with acid and halogen, while the high molecular homologues are either soluble only with very great difficulty or insoluble, and are no longer capable of reacting with acid and halogen.

The pure monomeres or the still low molecular acetylene polymeres are however because of their great liveliness in the presence of oxygen and because of the formation of compounds of a peroxide nature, rather explosive. But this lively course of reaction can be held within bounds by suitable operation or the formation of peroxide can be by-passed (indifferent gases, solvents, mixed polymeres).

FILM FORMATION

The knowledge of film formation is of the greatest importance for judging a paint medium, for, for every paint substance the problem consists in forming a film on the foundation, which according to circumstances must satisfy very special demands. Moreover these are very complex. They can not be discussed more fully here. A resin completely satisfying all demands, suited in every way for producing paint materials has not yet been created. The resin should be cheap as well as have the best qualities. Clear color, lustre, adhesive resistance, hardness, elasticity, resistance to abrasion, elasticity at low temperature, constancy towards water, alkali, acids, solvents, and non-inflammability are some of the stipulated requirements of a paint medium. As shown briefly above, numerous resinous products are available for forming film. The development of a film (a stiff skin of liquid) takes place in the case of a majority of these products by a **physical process.** The resin molecules or those of cellulose nitrate are already present in high molecular condition before they are employed for the preparation of lacquer. The solvent needed for solution evaporates, the solution is concentrated, and the result is the formation of a more or less good, tough film. In this process "softeners" play a not unimportant role. These films have great advantages, but certainly also a number of disadvantages (resolubility); the raw material of paint has in this process undergone **no chemical change** to speak of, and the film remains practically constant. The conversion of dissolved molecules into undissolved molecules is a **reversible** process.

$$\text{dissolved} \leftrightarrows \text{solid}$$
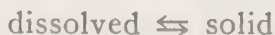
In contrast to this, the film-formation in the case of fat oxydative drying oils is the result of a chemical reaction. The substance present at first in the fluid state undergoes a **chemical change** and dries with a further chemical change more or less quickly to an insoluble, tough film.

The process of conversion
$$\text{liquid} \rightarrow \text{solid}$$

is usually **irreversible.** Standard for this conversion are the following various reactions:

1. The general cause is an oxydation; it is typical

for wood oil, linseed oil, and synthetic drying oils. Addition of drying substances (siccatives) further augment this oxydative reaction[18]). Meanwhile these additions may also interfere noticeably and lead to deterioration of the film qualities, as the oxydation once begun can go on and thereby enter the structure of the molecule.

2. A process of polymerisation and poly-condensation. The molecules oxydatively stimulated or correspondingly represented are polymerized or condensed autocatalytically and are gradually converted from the soluble low molecular hemi-colloid state by way of the mesocolloid to the high molecular state[19]). This conversion is connected with a rise of viscosity of the solutions of these substances.

3. A conversion from the two-dimensional to the three-dimensional molecular structure. This change involves diminution of solubility and an increase of fusibility of the substance. The viscosity, as far as solubility exists, thereby becomes practically higher.

To approach the processes taking place in film-formation of these chemically changed substances, it is of advantage to compare them with high molecular defined compounds which in their turn have originated in a more uniform reaction[20]).

POLYMERISATION AND POLYCONDENSATION

It is known that many organic molecules with double bonds can be polymerized. The arrangement of the double bonds is of great influence[21]). By polymerisation is generally understood those chemical reactions which, starting with small molecules, lead to larger molecules. If by-products appear from one or more substances in the course of this reaction, as for ex. water or ammonia gas, then we speak of polycondensation[22]). Both reactions must be stimulated. Catalysts, solvents, light, temperature, and pressure play a great role in this. For initiating the polymerisation of non-saturated compounds, the first requirement is the formation of a nucleus to start a chain reaction, in the course of which the molecule becomes larger. According to **Staudinger** the increase of the molecule may lead to threadlike and spherical compounds. The molecule goes on increasing until its energy (activating energy) is no longer adequate to accumulate further molecules.

Then the chain of reaction is broken. By what final groups the chains are terminated, is fairly unknown.

The reaction may cease by the accumulation of foreign substances with reacting power about the activated molecule, or probably also by the simultaneous occurrence of many similar parallel reactions[23]), for ex. fewer high molecular compounds originate by strong activation and also in condensation reactions. Peroxydic oxygen is said to cause formation of a nucleus and synthetic peroxides are said to be the producers of the polymeric reaction chain (Staudinger, Rieche).

$$
\begin{array}{l}
\quad\quad\quad\text{H} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \text{R H} \\
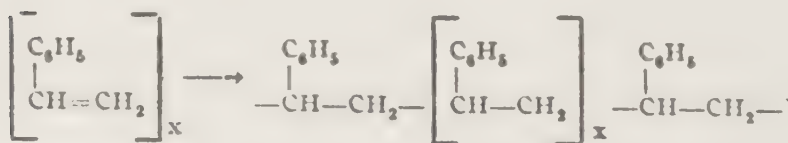\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \text{H H}_2\diagdown\diagup \\
\text{R—C—CH}_2\text{---} + \text{R—CH=CH}_2 \rightarrow \text{R—C—C}_2\text{—C—CH}_2\text{---} \\
\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad \text{O} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \text{O} \\
\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \\
\quad\quad\quad \text{O} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \text{O} \\
\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |
\end{array}
$$
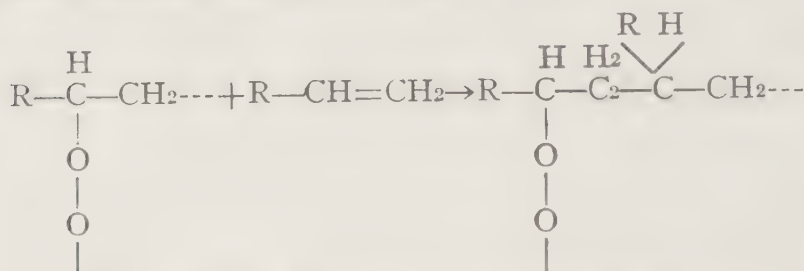
a) Threadshaped Molecules (Linear colloids).

For many macromolecular substances a threadlike form is characteristic. An example of a thread-shaped molecule is polystyrol, whose polymerisation can be conducted from low molecular up to high molecular compounds[24]).

$$
\begin{bmatrix} \text{C}_6\text{H}_5 \\ | \\ \text{CH}=\text{CH}_2 \end{bmatrix}_x \longrightarrow \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ -\text{CH}-\text{CH}_2- \end{array} \begin{bmatrix} \text{C}_6\text{H}_5 \\ | \\ \text{CH}-\text{CH}_2 \end{bmatrix}_x \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ -\text{CH}-\text{CH}_2- \end{array}
$$

The previously named pure synthetic resins originate also according to the kind of polymerisation of styrol. Thread-shaped polymeric molecules are formed also by polycondensation for ex. from glycol and succinic acid **(Carothers).**

$$
-\text{CH}_2-\text{CH}_2-\text{O}-\begin{bmatrix} \text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O} \\ \| \quad\quad\quad\quad\quad\quad \| \\ \text{O} \quad\quad\quad\quad\quad\quad \text{O} \end{bmatrix}_x -
$$

$$
-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{O}- \\
\| \quad\quad\quad\quad\quad \| \\
\text{O} \quad\quad\quad\quad\quad \text{O}
$$
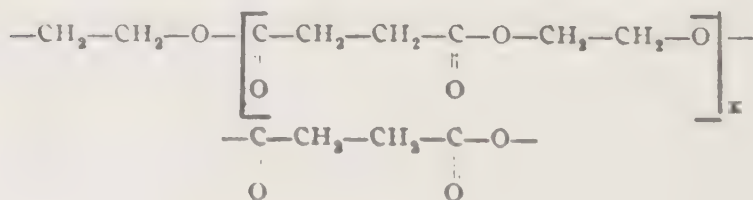
or also from p-creosol and formaldehyde.
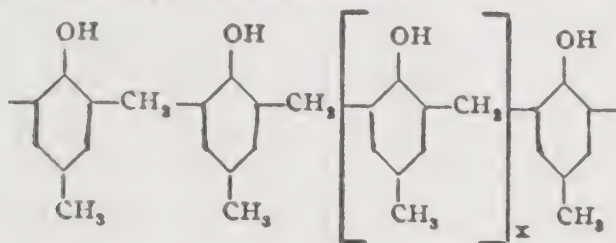
These elongated molecules have special physical properties, such as elasticity, toughness, solubility, a melting point increasing with the length of the molecule and increasing viscosity of the solutions, unlimited capacity of swelling, no great hardness, and perhaps further capacity for polymerisation or condensation (can be hardened).

Thread-shaped molecules can also enter mutual combinations in various positions, which then lead to reticulated molecules in which firm bonds, so to speak, are present along side of weaker ones. The higher elasticity of certain macromolecular molecules is based in some cases on this cooperation. **Staudinger** has described a reticulated high molecular molecule of this kind[25]. The polymerisation of styrol in a mixture with varying quantities of divinyl benzol under circumstances suited to styrol leads to products different from the pure polystyrols. Divinyl benzol can by means of both of its vinyl groups enter a double reaction with styrol and by this means react somewhat according to the following scheme (Cf. Fig. 2):


Fig. 2.
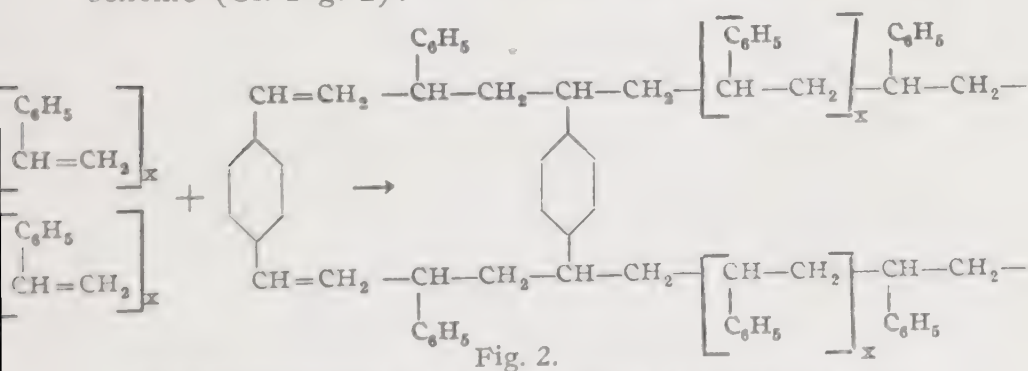
The participation of divinyl benzol in styrol polymerisation is also clearly noticed in the change of physical properties of the polymeric products obtained. Partly reticulated macromolecules are not merely present in this styrol divinyl polymerisate but surely also in vulcan-

ized caoutchouc and in the product of phenol formalde-
hyde condensation, "resitol". In the first case the sulphur
atoms (also oxygen atoms), in the second case the
methyl groups hold the reticulated molecule together.
The reticulation of threadlike molecules necessitates:
diminution of solubility, generally an increase of vis-
cosity of solutions, increase in hardness, and elasticity
peculiar to caoutchouc, increase in capacity of swelling,
further capacity for polymerisation and condensation
(for ex. capacity of resitols for being hardened).

SPHERICAL MOLECULES (Sphero-colloids)

If the number of reticulation places increases with-
in the polymeric molecule, the compound loses thereby
more and more of its special character as a threadlike
molecule and increases in three dimensions while form-
ing exculsively firm bonds. The so-called three-dimen-
sional molecules possess in spite of their very high mole-
cular weight physical qualities completely different from
those of the thread-shaped molecules. Thus this reaction
generally leads to insoluble, unfusible, chemically very
resistant, very hard, slightly elastic, non-swelling pro-
ducts incapable of further hardening. If soluble spherical
molecules are successfully produced, these particles be-
have like latex particles as regards their viscosity. An il-
lustration of a high molecular compound of spherical
structure is poly-divinyl benzol[26]).
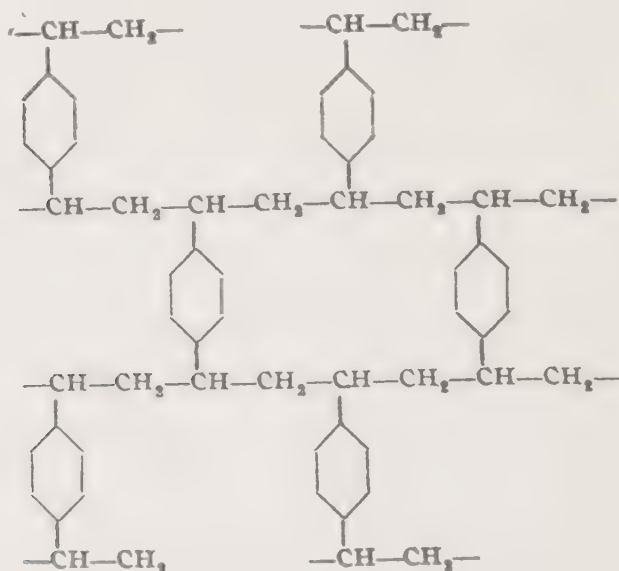
An analogous compound is no doubt vulcanite and the hardened product of phenol-formaldehyde-condensation resit[27]). Cf. Fig. 3
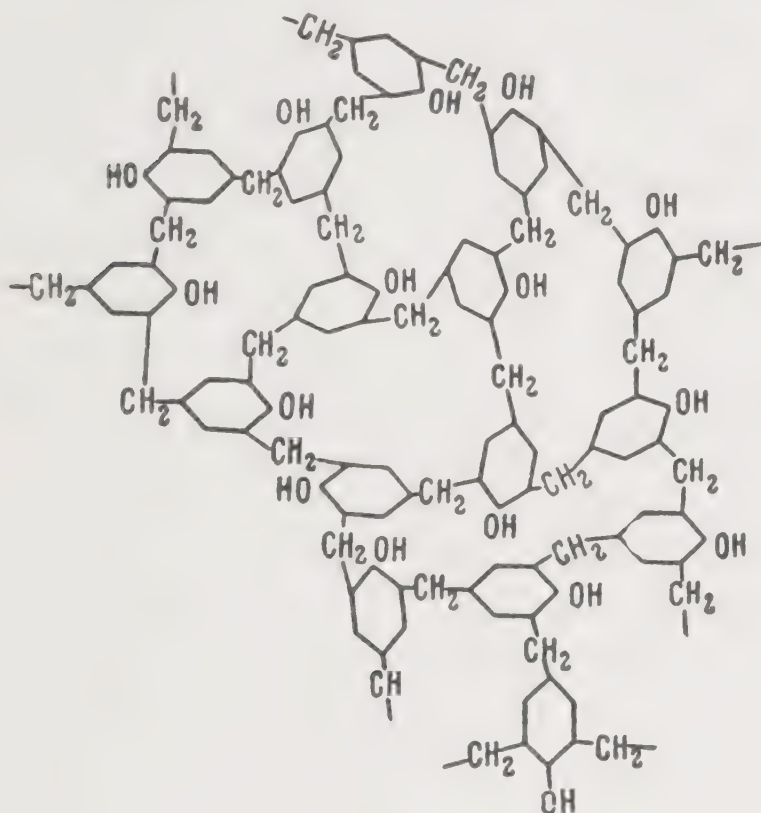
FIG. 3

THE FILMING OF DRYING OILS

By the drying of oils, as said, various superimposed reactions take place. Oxydation leads as a first reaction to the formation of peroxides, as can be determined by numerous observations. This formation of peroxide certainly begins first with a double bond of the residue of sebacic acid, or with CH_2 groups especially activated by means of their arrangements. According to the constitution of the oil the course of the drying process differs. In the case of the influence of oxygen on a CH_2 group this can perhaps be oxydized to a keto-group, or the oxygen intervenes between the carbon and the hydrogen in the manner of a peroxide (Rieche). The active oxygen that has entered the molecule can then give rise to very manifold reactions. Thus scissions of

C-C unions may occur or the oxygen can lead to further oxydation reactions (decomposition, formation of low molecular acids). These peroxydic oxydation processes can also lead to systems which have now attained a higher capacity for polymerisation. A CH_2 group especially favorable for an attack by oxygen is present in ricinoleic acid. By suitable treatment this acid can be converted into a coordinate twofold nonsaturated acid (Scheiber's acid), which lends the corresponding tri-glyceride the capacity of drying well[28]).

$$—CH=CH—CH_2—CH— \rightarrow —CH=CH—CH=CH—$$
$$| $$
$$OH$$
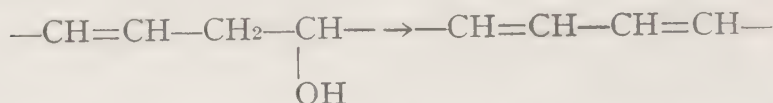
But if the oxygen reacts with the double bonds already present in the sebacic acid molecules, there probably takes place the formation of compounds like:
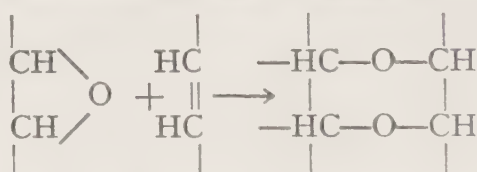
$$—CH — CH—$$
$$—CH=CH—+O_2--- \diagdown \diagup$$
$$O—O$$
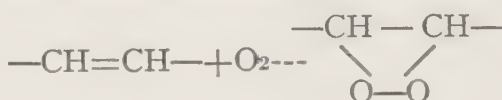
These compounds can now react with non-saturated compounds of other molecules of sebacic acid and so introduce a reticulation **(Blom, Rieche).**

$$
\begin{array}{ccc}
| & | & | \qquad | \\
CH\diagdown & HC & —HC—O—CH \\
| \quad O \; + \; || \longrightarrow & | & | \\
CH\diagup & HC & —HC—O—CH \\
| & | & | \qquad |
\end{array}
$$

Whether by this means a much higher molecular molecule reticulated by oxygen is formed, is still uncertain (oxines). To be sure peroxides possess the capacity of being polymerized[29]). In this natural process of oil drying we have a reaction similar to that in the vulcanisation of caoutchouc or in the concatenation of polystyrol by divinyl molecules.

Meantime peroxides have, as mentioned in connection with the polymerisation of a non-saturated compound, the effect of hastening polymerisation. By these peroxides is introduced the polymerisation of non-saturated compounds present or reproduced. The polymerisation of oil leads to thickening (stand oils).

The polymerisation of drying oils in spite of double bonds probably does not take place for the most part in the manner of styrol, as the residue of non-saturated

sebacic acid present in them is composed of long alkyl-chains. It is known that capacity for polymerisation of symmetrical ethyl- and butadiene derivatives decreases. For the tri-glycerides, according to more recent viscosity and Röntgen measurements[31]) a sprawling form is assumed. A chain formation for a coordinate non-saturated tri-glyceride could only be imagined as something like this,

$$
\begin{array}{cc}
\text{---CH—CH} = \text{CH—CH---} & \quad \text{---CH—CH} = \text{CH—CH---} \\
\mid \qquad\quad \mid & \qquad\qquad \mid \qquad\quad \mid \\
\text{R} \qquad\quad \text{CO} & \qquad\qquad \text{CO} \qquad\quad \text{R} \\
\mid & \qquad\qquad \mid \\
\text{O} & \qquad\qquad \text{O} \\
\mid & \qquad\qquad \mid \\
\text{CH}_2 \text{——— CH ——— CH}_2 \\
\mid \\
\text{O} \\
\mid \\
\text{CO} \qquad\quad \text{R} \\
\mid \qquad\qquad \mid \\
\text{---CH—CH} = \text{CH—CH---}
\end{array}
$$
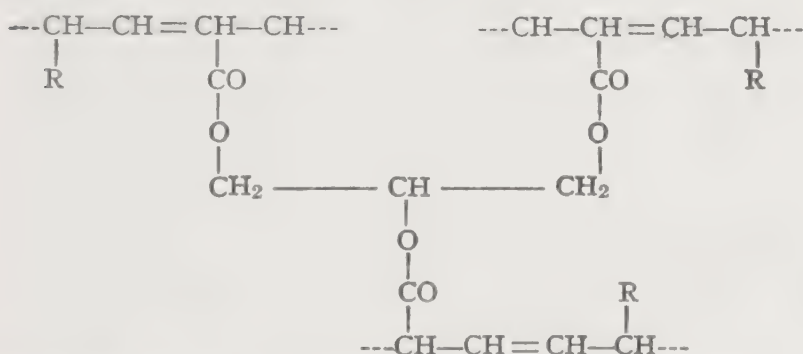
but from the first named reasons they can scarcely be considered actual. Probably the faty oils have not the capacity of chain-forming polymerisation. Meantime it has been found that non-saturated residue of sebacic acid in tri-glycerides can react mutually according to the Dien synthesis[32])

$$
\begin{array}{l}
\text{CH}_3\text{—(CH}_2)_3\text{—CH} = \text{CH—CH—CH—CH} = \text{CH—(CH}_2)_7\text{—COOR} \\
\qquad\qquad\qquad\qquad\quad / \qquad\qquad \backslash \\
\text{CH}_3\text{—(CH}_2)_2\text{—CH} \qquad\quad \text{HS—CH=CH—(CH}_2)_7\text{—COOR} \\
\qquad\qquad\qquad \backslash \qquad\qquad / \\
\qquad\qquad\qquad\quad \text{CH=CH}
\end{array}
$$
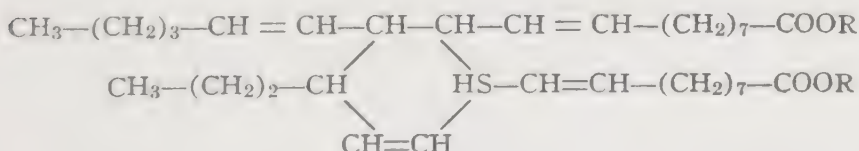
and thereby give rise to a concatenation and reticulation. The combination of various tri-glyceride molecules after a similar process leads then to a thickening and continued strengthening of the oil film. By the increase of these reticulated positions arise the physical and chemical properties typical for high molecular compounds. These reticulations can be considered as an intra-molecular and extra-molecular polymerisation.

SYNTHETIC, OXYDATIVE DRYING OILS

For the knowledge of oil-drying of synthetic oxydative drying oils it is of considerable significance to know the relationships between oxydation and polymerisation. It is known that more stable and tougher films originate from slow drying of fatty oils than by quick drying.

Thereby time is granted the individual molecules for chain reactions and the formation of larger molecules is furthered.

As already mentioned, acetylene derivatives can be excellently polymerized. Chain formation is favored by the reactive vinyl group (Cf. Fig. 1a and 1c). As long as chain formation takes place by poly- merisation, no exact analogy can be given with oil drying in general, at most with the formation of stand oil, particularly that of wood oil, since here, as mentioned, the coordinate double bonds might perhaps favor this kind of polymerisation. The possibility of auto- oxydation is furnished by the double bonds still pre- sent. Here the way is especially prepared for the forma- tion of peroxides and the conversion into polymeric oxides. Thus here too polymeric products occur in which the individual or polymeric molecules are united to larger, three-dimensional structures by connecting oxy- gen which are insoluble (Cf. Fig. 1b). The assumption of a Dien synthesis is also admissible here. Not until after the formation of such compounds, does the product lose its capacity for reaction, become stable, undepoly- merizable, and thereby form irreversible films[33]).

Products will be obtained with better physical prop- erties the larger the molecules formed. In this the for- mation of two-dimensional molecules is shown to be superior to that of three-dimensional; for in three-dimen- sional macromolecules the brittleness of the films in- creases and their adhesive resistance is considerably de- teriorated.

Synthetic oxydative drying products especially suited for paint purposes with great adhesive resistance and still of sufficient hardness and other physical and chemical properties required are best obtained by considering the good properties of natural drying oils. These synthetic products must be given the possibility of forming auto- catalytic threadlike molecules of considerable length at an ordinary temperature and then of converting by par- tial molecule reticulation into insoluble reticulated mole- cules only slightly brittle. For these stipulations the synthetic oxydative drying oils form the worth-while be- ginning of a great development.

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PRINCIPLES OF THE
PROCESSES OF POLYMERISATION

In this work the development of the chemistry of high molecular substances is to be sketched in broad strokes. No complete survey of the realm of high molecular compounds is offered but the treatment is limited to those specially formed by polymerisation. The present section treats principally of the processes of polymerisation, the different kinds of polymerisation, the relation between the constitution and the capacity for polymerisation, and finally the influence of the substituents on the capacity for polymerisation of non-saturated organic compounds. Products arising from the polymerisation of acetylene, or ethylene, and their derivatives or carbonyl compounds will chiefly be treated, as they are of the greatest interest both in a scientific and a technological respect.

I. DEVELOPMENT OF THE CHEMISTY OF HIGH MOLECULAR ORGANIC COMPOUNDS

It was already known in the last century that many chemical reactions do not yield final products of a crystallized form. Many of these uncrystallized and viscous substances were gathered together under the name of "resin". Thus the name was frequently used for something undesired, harmful, and of little value. Originally only a group of natural products was designated by the word "resin". As many times scarcely no differences exist in normal properties between natural resins and the products resulting from chemical syntheses, the use of the same designation is justified for both classes. Complaint has often been made in the literature of the appearance of resinous by-products, for ex. by A. v. Bayer during the condensation of phenol and formaldehyde. With regard to many organic non-saturated compounds (styrol, acrolein, vinyl compounds and others) it has been known for many years that they are polymerized by the influence of light and warmth. But it was not known what to do with these substances and an investigation of the formation of these synthetic resins and products of polymerisation was neglected, especially as in their investigation normal methods of clarifying the constitution according to organic chemistry apparently failed. In the older organic chemistry these products were no doubt designated as high molecular although no

well-founded statement could be made about their molecular weight. The assumption that high molecular products are present, rested on the fact that these substances have quite other properties than substances of similar structure with low molecular weight.

In the course of the last decades substances of resinous constitution have been added to these undesired byproducts in increasing numbers, purposely produced by exploitation of numerous, empirically determined reactions of organic compounds. Their development, range, significance, and improvement is today the province of the chemistry of synthetic substances[1]).

The investigation and the chemical clarification of the constitution of natural products, such as albumin, cellulose, caoutchouc etc., also high molecular compounds generally not crystallizing, began earlier. The effort has always been made to become better acquainted with these compounds which nature very often constructs from the simplest components in an astonishing way, and finally to produce them synthetically. Technology and science were more and more interested in these substances without however really knowing the closer relationships of their origin and their molecular structure. In the consideration and treatment of all high molecular compounds, reliance was placed on views applicable to the many thousand organic crystallizing, low molecular substances. By manifold theories the attempt was made to interpret the structure and the physical properties observed of these natural and artificial products. Meanwhile it was also mentioned that the physical state of an organic compound is dependent both on its chemical constitution and on the manner of the arrangement in space of the simplest components within the great complex. When "reaction type groups" are not present at the beginning, nevertheless definite reactions later produce such groups. Such typical groupings in the origin of resins were assumed. As already mentioned, even many well crystallized and chemically pure substances are actually capable of later conversion into resin in the presence of corresponding groups by definite reactions.

Thus, for example, ortho- and para-oxy- benzyl alcohol undergoes by prolonged heat a change into a chiefly soluble and fusible resin, which then further changes into an insoluble, non-fusible product[2]). Here then a uniform substance assumes manifold resinous conditions. Polymeric compounds, originating from non-saturated

compounds received early attention. From the constitution of such synthetic polymeres no idea could at the beginning be obtained of their treatment. Many high molecular compounds have been eagerly investigated especially from the point of view of their colloid constitution without however entering on the interesting and important question of what elements such molecules are composed and what are the causes of this polymerisation. Often false conclusions were drawn from such one-sided investigations.

The consideration of these natural and polymeric products gave rise more and more to the basic question whether such an enlargement of the molecule, that is a polymerisation, takes place in the manner of a chemical reaction or of a physical process. Investigations in colloid chemistry led to the view that high molecular substances represent no structure to which the classical idea of molecules could be applied in all its inferences. It was often believed that these polymeric compounds did not have a structure such as low molecular compounds have, but that here a physical process, called **aggregation,** led to an enlargement of the particles the result of which was called a **micelle.** That the majority of these polymeric compounds are to be considered as particles in which all the atoms are united by principal valences, that is as in low molecular organic compounds, for ex. paraffin hydrocarbons, **H. Staudinger** was the first to be able to show in numerous works[3]).

Still there are considerable differences between the low and the high molecular organic compounds in respect to physical properties and chemical structure along with great similarity, these differences requiring different treatment and manipulation of these substances.

H. Staudinger reports the following with regard to these relationships[4]):

"If I am able to report today with regard to further progress in this field in the last ten years, I would like this time to call the survey 'Regarding macromolecular chemistry'; for today it is necessary to emphasize not only the common relationships existing between high and low moleculars in their structure, but also first of all **to distinguish what is special and what is individual which differentiates macromolecular chemistry from the chemistry of low moleculars, and makes necessary a separation of these two provinces in the frame work of organic chemistry.**

"Classic organic chemistry has previously busied it-

self chiefly with investigation of low molecular sub-
stances: Of the 300,000 organic compounds known today
the majority have a molecular weight below 1000 and only
a few have one of perhaps as high as 4000. The number
of atoms forming such molecules is comparatively
slight.

"It is a different matter in the case of the high mole-
culars. Here are substances whose molecules are com-
posed not of a few hundred atoms at most, but of thou-
sands, tens of thousands, and perhaps even of millions
of atoms. These macromolacular substances present
the chemist with entirely new problems: first the repre-
sentation of these substances is different, second the
clarification of their constitution, and finally their whole
chemical and physical behavior". These differences are
further indicated in the following table.

In the investigation of polymeric compounds of this
kind one must first answer the questions about the com-
ponents (monomeric molecules), the manner of their
union, and the size and form of these particles.

An important problem for estimating a chemical
compound is the determination of molecular weight.
In the case of the high molecular compounds new pos-
sibilities must be sought for this. In the case of soluble
high polymeric compounds the colloid properties of these

Table I

Differences between low and macromolecular compounds

	Low Moleculars	Macromoleculars
Molecular weight	< 10000	> 10000
No. of atoms in a molecule	< 10000	> 1000
Substances consist of	uniform molecules	polymeric uniform molecules
crystal structure	Molecule lattice	Macromolecule lattice
Solution	Molecular solution mono-dispersed	Macromolecular solution=colloid solution
Production by	Synthesis	Polymerisation, poly-condensation.

substances or their derivatives in dissolved form can
be called upon[5]. So the molecular weights of many
natural and synthetic high molecular compounds could
be determined by viscosity measurements. By the deter-
mination of resulting groups in the high polymeric mole-
cule of poly-oxy-methylene it first became known
through chemical methods that polymeric molecules are
actually constructed in the manner of a low molecular
compound and have predominantly a **chain- or thread-
shaped form.** This knowledge was then applied in the
investigation of numerous synthetic high polymeric sub-
stances and also recognized as basic in the structure of
natural high molecular substances. These polymeric
particles are therefore not miscellas, but molecules in
the sense of classic organic chemistry[6]), which fact could
also be determined by numerous Röntgen measurements.
The special physical properties such as toughness, elas-
ticity, capacity of forming film or fibre, stability, resis-
tance to water and chemicals, or hardness of these poly-
meres, partly very high molecular substances, are not de-
termined by the kind of basic molecule, but progressively
by the size and form of these high molecular particles.
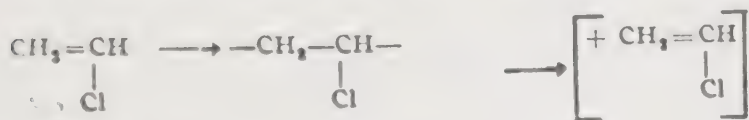
THE MECHANISM OF POLYMERISATION

By polymerisation is designated the union of several
molecules of a compound into a product with a com-
position of the same percentage but with a multiple of
the original molecular weight. The process of polymeri-
sation takes place by the satisfaction of free valences
or of residue valences, conversion of unstable ring-sys-
tems or by a migration of hydrogen (polymerisation by
dehydrogenation, condensing polymerisation). An in-
clination to polymerisation is shown both by compounds
with double bonds and $C=C$, $C=O$, $C=S$, also $C=N$
among others, like ethylene oxide, peroxide, ozonides,
lactones. Distinguished from polycondensation, for ex.
the formation of poly-ester from oxyacids, no water,
ammonia, hydrogen sulphide, chloric or bromic acid are
separated during this reaction. The measure of a poly-
merisation fluctuates within wide limits. "Dimeric",
"trimeric", and "tetrameric" products of many products
are known, as well as low polymeres (hemi-colloids of
a molecular weight approximately 4-10000 according to
Staudinger, middle polymeres(meso-colloids of a mole-
cular weight approx. 10-70000) and high polymeres (eu-
colloids of a molecular weight of approx. 70000 to 1,000,-

000). In rare cases polymerisation leads to products of merely the same molecular weight. High polymeric products ordinarily contain various large complexes in a close mixture. The state of resin, for instance, is itself to be attributed to a mixture of substances in a polymerisation that has not advanced far. It is understood at the beginning that these substances will be more stable and defined, the more the individual components are similar in kind chemically and physically. The special character of high polymeric substances lies in these manifold possibilities of reaction. The conversion of nonsaturated monomeric substances into polymeres can take place basically in different ways, whereby the final product is dependent on the kind of reaction. In many cases however it is difficult to distinguish clearly between the different individual kinds of reaction.
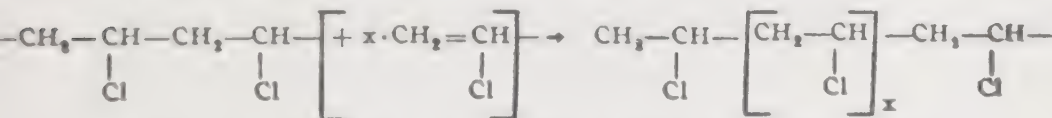
CHAIN POLYMERISATION

The process of polymerisation leading to **important high molecular** products, takes place generally by **chain polymerisation.** This reaction is comparable to the well-known chlorine-detonating gas—chain reaction. By this single molecules of the non-satisfied compound in question are activated, thus made capable of accumulating new molecules[7]). Thereby arise new molecules with active final-groups. The process of polymerisation then continues until a breaking of the chain occurs by a secondary reaction or by cessation of activity[8]).

CHAIN POLYMERISATION OF VINYL-CHLORIDE

$$CH_2=CH \atop Cl \longrightarrow \begin{matrix} -CH_2-CH- \\ | \\ Cl \end{matrix} \longrightarrow \left[+ \begin{matrix} CH_2=CH \\ | \\ Cl \end{matrix} \right]$$

vinyl chloride   activated molecule

$$-CH_2-CH-CH_2-CH- \atop Cl \quad Cl \left[+ x \cdot CH_2=CH \atop Cl \right] \rightarrow CH_2-CH- \atop Cl \left[CH_2-CH \atop Cl \right]_x -CH_2-CH- \atop Cl$$
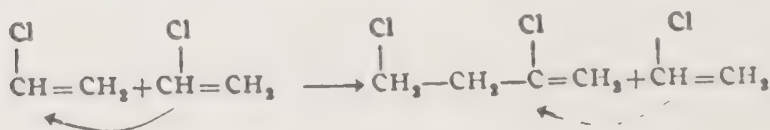
Here no migration of hydrogen atoms or other atoms takes place, nor is there any separation from groups of a different kind. According to the process of the reaction average smaller or larger high molecular particles are formed. Low molecular products of polymerisation do not arise in this kind of polymerization.
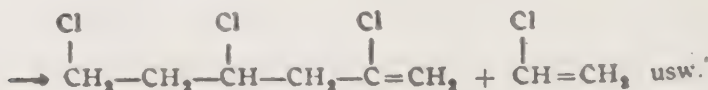
CONDENSING POLYMERISATION[9])

It can be imagined however that the formation of active molecules does not take place and that a non-saturated molecule joins another by the **migration of hydrogen,** so that finally as the reaction progresses polymeric products also originate. From the course of this reaction it is assumed that here dimeric and trimeric, that is low molecular intermediate products, must arise, with the further capacity of reacting with further monomeric molecules by enlargement of the molecules. This process can be expressed in a formula as follows:

Condensing Polymerisation of Vinyl Chloride

$$CH = CH_2 + CH = CH_2 \longrightarrow CH_3 - CH_2 - C = CH_2 + CH = CH_2$$

mobile hydrogen atom

$$\longrightarrow CH_3 - CH_2 - CH - CH_2 - C = CH_2 + CH = CH_2 \text{ usw.}$$

Actually there is a series of substances in which a reaction process of this kind takes place and in which intermediate products are successfully seized. In how far then the formation of polymeric compounds proceeds according to the one or the other or both of these kinds of reaction, is attributed to definite influences already exerting influence on the monomeric product. As in the course of this polymerisation no loss of substance occurs, that is, no separation of water, ammonia, etc., as in the case of the condensation reactions, but merely a migration of hydrogen among the molecules, a reaction process of this kind is often called **false polymerisation.**

The requisite for every polymerisation is, as said, the presence of a non-saturated group or the possibility of forming one in the midst of a reaction. Non-saturated groups are found in more or less decided form in hydrocarbons, aldehydes, alcohols, acids, esters, ethers, lactones, nitriles, isonitriles, salts of non-saturated organic acids and other compounds. By heating, cracking, lighting, dehydrating, compounds originally incapable in themselves of polymerisation can often be converted into polymerisable compounds. Such processes occur in nature and today are already applied to technology[10]). By these partial reactions the rapidity of polymerisation can be

increased. But these extended conversions are not cala-
lytic processes. That is to say, that although the same
non-saturated condition is present in many substances,
nevertheless the compounds possess variously great ca-
pacity for and rapidity of polymerisation. Precisely as
definite isomeric forms or substituents in low molecular
substances are of definite, indicative, strengthening or
weakening influence, so the capacity for polymerisation
of a compound does not depend solely on the structure
of a molecule, but the influence of the substituents on the
capacity for polymerisation of non-saturated compounds
is very often considerable[11]). These relationships will
be considered later.

The rapidity of polymerisation is determined by the
properties of the molecule in question, and there exist
possibilities of introducing the reaction by outward in-
fluences, of increasing, directing, slowing, or stopping it.
For this we have so-called **activators (catalysts,** regula-
tors, buffers') and **anti-catalysts.** In the technological
production of high molecular compounds it is necessary
to control the various exothermic polymerisation reac-
tions taking place in a lively or even violent manner,
to stop them at a desired degree of polymerisation or
generally to take it so far. Only by direction and control
of such different processes has technology become able
to produce definite and uniform polymerisates and poly-
condensates. **The rapidity of polymerisation** is influ-
enced chiefly by warmth, pressure, light, and catalysts.
Polymerisation takes place spontaneously in many
non-saturated compounds in the cold or only when
heated, for ex. in the case of formaldehyde, styrol,
acryl ester. Light favors for ex. the polymerisation of
vinyl acetate, vinyl chloride, and vinyl bromide. But
many compounds are only converted into polymeric
compounds by catalysts. These catalysts are exceedingly
numerous, and by means of them the polymerisation
can be accelerated and influenced in many cases aston-
ishingly, just as by heat of various degrees or by light of
different wave-lengths. Thus, for ex. styrol can be
converted into distyrol by definite catalytic agents,
while with spontaneous polymerisation or by using
other catalytic agents of high molecular polystyrols are
obtained[12]). A different process of polymerisation of this
kind is also known in the case of butadien. The catalysts
mostly employed are: peroxides, such halides of metals
and metaloids as have the tendency to change into com-
plex compounds, also acids, bases, metals, active earths

and others. Polymerisation is caused even by slight additions of polymeric to monomeric parts (carbon, nuclear catalysis[13]). Non-saturated compounds only polymerized by catalysts are for ex. isobutyls, enethole, indene, propenyl benzole, ethylene oxide. Many substances are not influenced by peroxide-like, strongly acid or complex catalysts, but by those with a weak basic or slightly acid character; for ex. polymerized ethylene oxide with calcium hydroxide and various other earthy potash salts.

The manner of conducting the polymerisation has great influence on the course of the polymerisation. Without doubt, the temperature at which it is conducted is decisive. A product polymerized in solution or in emulsion is generally very different from the pure polymerisate and ordinarily shows a different average degree of polymerisation (artificial latices). The concentration of a solution or the continuous addition of monomeric products likewise determine the course of the polymerisation and the physical properties of the accruing polymeric products. Actually the influence of the solvent plays an essential part here just as in other chemical reactions[14]), for ex. in the polymerisation of butadien by means of lithium in benzol chiefly a 1-2-addition occurs; while working in ether in a far greater quantity the 1-4-addition is demonstrable[15]). At any rate, in this respect also, high or low temperatures employed in the polymerisation of butadien are of very decisive influence.

Many of the high molecular compounds used in technology today are produced according to methods and view-points mentioned here in part.

It is technologically very important that a polymerisation process should be delayed or even stopped by definite additions. If it is a question of obtaining easily polymerisable compounds by storing or distillation in a monomeric state, the so-called **anti-catalysts (stabilizers)** are used. The manner in which such substances act, as for ex. univalent or polyvalent phenols iodine, sulphur, metals or metal salt, is in detail still quite unknown (styrol can be obtained by slight additions of sulphur or hydroquinone in a monomeric state). However the most conspicuous effect is the probable repression of autoxydation and the formation of peroxidic intermediate compounds which are said to yield in especial degree the reaction nuclei for a beginning chain of polymerisation.

The reverse of polymerisation is **depolymerisation.** In contrast to polymerisation, depolymerisation is a freeing of the atom combinations of organic molecules. The ease with which a definite compound is freed by a chemical intervention depends first of all upon the kind of atoms united by it. Often in depolymerisation it is a question of freeing C-H, C-O, C-N, and especially C-C-unions. Much more easily freed are O-H- and N-H-unions. In the depolymerisation of paraffins (cracking) or polystyrol and of many high molecular products it its a question particularly of the freeing of this most constant union. By the same influences required for polymerisation, as for ex. by warmth or catalysts the monomeric compounds can be more or less completely reformed. In dealing with the composition of high molecular compounds about molecules with threadlike structure, this reversible process of a monomeric $\leftrightarrows$ polymeric molecule is possible rather than in the case of molecules of so-called three-dimensional or spherical form. Not merely do monomeric and dimeric parts arise in cracking of these three-dimensional macromolecules, but also a considerable quantity of new aliphatic or aromatic, saturated or non-saturated compounds according to the way the molecule in question is built up and the depolymerisation of resit[16]), a three-dimensional macromolecule, in an atmosphere of hydrogen, phenol, cresol, benzol. toluol are produced as well as considerable portions of aromatic polynuclear compounds with a higher boiling point of the resitol type, while in the cracking of polystyrol or polyacryl esters practically without exception only the monomeric compounds are recovered.

In considering the constancy of high molecular organic compounds of threadlike or spherical form, a not unessential difference can easily be determined. While threadlike molecules depolymerize the more easily, the longer their particles, the three-dimenesional molecules become more constant by increasing spherical form along with other influences also in the presence of heat.

III. VARIOUS TYPES OF POLYMERISATION PRODUCTS

Many substances are inclined both towards **polymerisation and polycondensation**[17]), for ex. formaldehyde. aldehyde, oxystrol, vinyl alcohol, now-saturated sebacic acids, and others. However, there are principal differences between the two kinds of reaction[18]). In polymer-

isation and polycondensation we find along with the formation of **threadlike, polymeric molecules** of varying degrees of polymerisation (linear colloids according to **Staudinger),** also processes which may lead to ring-formations and open branches or to partial reticulation of individual thread molecules and finally to spherical macromolecules (sphero-colloids). For example, the conversions, of formaldehyde of every kind are worth mentioning here.
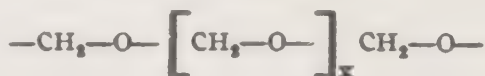
By condensing polymerisation[19])

$$HO-CH_2-OH+CH_2=O + X \cdot CH_2O \longrightarrow$$

mobile oxygen atom

$$HO-CH_2-O-\left[CH_2-O-\right]_x CH_2-OH$$
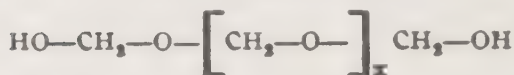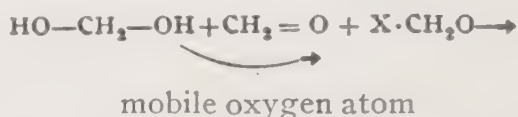
or according to the kind of chain polymerisation, which might be represented by the following formula:

$$CH_2=O \longrightarrow -CH_2-O- \qquad + x \cdot CH_2O \longrightarrow$$
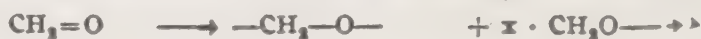
formaldehyde   activated molecule

$$-CH_2-O-\left[CH_2-O-\right]_x CH_2-O-$$

poly-oxy-methylene

are formed low and high molecular poly-oxy-methylenes of threadlike or branched formed or low molecular rings, as for ex. tri-oxy-methylene

$$CH_2 \left\langle \begin{matrix} O-CH_2 \\ O-CH_2 \end{matrix} \right\rangle O$$
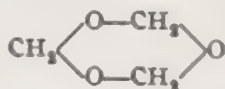
A further interesting kind of formaldehyde concatenation ,also a condensing polymerisation, is that consummated under the influence of weak alkalis. From this arises a quantity of sugars,
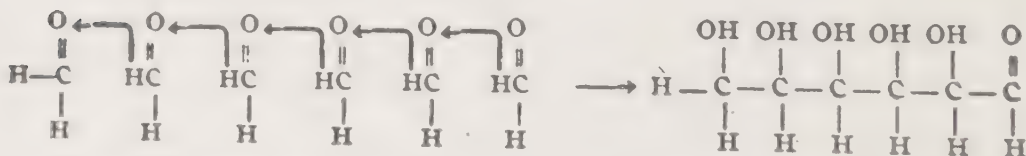
mobile oxygen atoms   hexose (sugar)

formed from aldehyde by a continuous aldol condensation.

In the conversion of formaldehyde with phenol after the manner of a condensation there are formed accord-

ing to the ratio phenol: formaldehyde, low or high molecular **novolaks,** but with an excess of formaldehyde **resitol** or finally **resit**[20]). The ratios of polymerisation clearer in detail are often wiped out, as frequently basically other ratios arise by conversion of individual forms of condition.

The production of polymeric products can be started with one or several non-saturated compounds; also substances may be employed which have only obtained the capacity for polymerisation by means of secondary reactions. As the majority of hydrocarbon compounds possess no polar opposites among the atoms of their structure, that is. are homeo-polar, as for ex. hydro-

Table 2.

Natural and synthetic high molecular compounds formed by different kinds of polymerisation.

Kind of polymerisation	natural homeo- and heteropolar high polymeric compounds and derivatives	synthetic homeo- and heteropolar high polymeric compounds
isopolymerisation	caoutchouc chlorocaoutchouc cellulose acetate cellulose starch albumin	polystyrol polyvinylchloride polyvinyl acetate polyoxymethylene polyvinyl alcohol polyacrylic acid.
mixed polymerisation	cellulose mixed ester and ether	polyvinyl acetate-polyvinyl chloride polystyrol-polydivinylbenzol polyvinyl chloride-polyacrylic acid ester polystyrol-polyacrylic acid nitril
hetero-polymerisation	cellulose xanthogenate solution	polyvinyl acetate maleic acid stilben maleic anhydride
dehydro-or hydropolymerisation	biological processes, oil drying	formation of resins from saturated and non-saturated aliphatic and aromatic com'ds for ex. from tar oils

carbon, chlorine derivatives, ester, ether, and partly also alcohols, other ratios are present in the hetero-polar organic compounds, as for ex. in genuine acids, bases, and salts. By employing homeo- or hetero- polar organic compounds for polymerisation, the physical properties of the polymeric substances resulting can be considerably influenced. For the essentially different physical properties of the classes of compounds named in monomeric as in polymeric condition, there are examples in natural and synthetic products. Thus for ex. homeo-polar high molecular compounds like caoutchouc, chloro-caoutchouc, cellulose acetate, polystyrol, and poly-vinyl-chloride are dissolved in organic solvents and not in water; on the other hand hetero-polar high molecular compounds such as albumin or polyacrylic acid can be converted into solution with water.

According to these view-points and especially according to the kind of polymerisation perhaps three types can be distinguished. Some essential representatives of natural and synthetic high molecular compounds are cited under these view-points in the foregoing table.

1. Isopolymerisation.

The conversion of **uniform products capable of polymerisation** into polymeres is probably the usual kind of polymerisation. Here analogous basic molecules range themselves together within the chain-formed, branched, or spherical molecule, for ex. in the case of polystyrol[21]);

$$C_6H_5 \qquad\qquad \left[\begin{array}{c} C_6H_5 \\ | \\ CH-CH_2 \end{array}\right]_x \qquad C_6H_5$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$-CH-CH_2- \qquad\qquad\qquad\qquad -CH-CH_2-$$
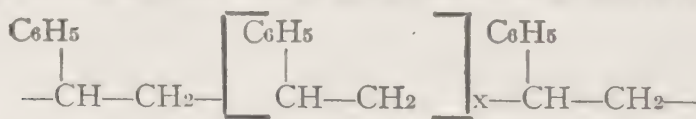
The physical properties of the polymeric compounds correspond to those of the basic molecule, but are chiefly determined by the structure and size of the polymeric molecules. Such isopolymeric products have been known in great number in recent years and have been produced in increasing quantity for various technological purposes.

2. Mixed polymerisation.

High polymeric compounds arise not only by polymerisation of a non-saturated basic molecule, but two or several basic molecules **of different kind** can be joined to a new polymeric molecule. The structure of the molecule is mostly chain-formed, the sequence usually alternating. The mixed polymerisates do not have the same qualities

which should perhaps arise from the mixture of the polymeres. On the other hand new, uniform substances are formed with new specific properties, since here it is not a question of polymeric mixtures but of mixed-polymeric substances. By abundant possibility of combination and because of new specific properties, such synthetic products find application where previously isomeric products were unfavorable or unsatisfactory. In many cases mixed polymerisation leads with unexpected rapidity to completely insoluble high molecular compounds or to those still capable only of swelling. This occurs especially when polymerisable compounds, provided at least with non-saturated groups, can form themselves into threadlike molecules, in order so to contribute to strongly defined molecule branches. To be sure, this requires a certain agreement in the constitution of the compounds to be polymerised. The cross connections occuring here and there very often require a heightening of the caoutchouc-like elasticity within the synthetic substances. In this way the mixed polymerisation of styrol with divinyl benzol and that of divinyl acetate with divinyl ether leads to insoluble, elastic high molecular products.
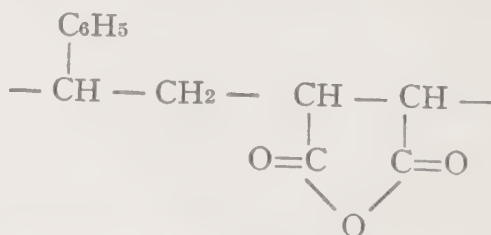
In **normal mixed polymerisation** there is joining of two or several basic molecules, each one of which is itself polymerisable. Imagine, for instance, a mixture or emulsion of monomeric acrylic acid nitril and styrol, monomeric styrol and divinyl benzol, or monomeric vinyl acetate and vinyl chloride; each individual substance is poly-

$$
\begin{array}{l}
\text{Cl} \\
| \\
\text{CH}{=}\text{CH}_2 \; + \; \text{CH}{=}\text{CH}_2 \; \longrightarrow \\
\text{vinyl chloride} \quad | \\
\qquad\qquad\qquad \text{O} \\
\qquad\qquad\qquad | \\
\qquad\qquad\qquad \text{CH}{-}\text{CH}_3 \\
\qquad\qquad\qquad \text{vinyl-acetate}
\end{array}
$$

$$
\begin{array}{l}
\qquad\quad\;\; \text{Cl} \\
\text{Cl} \qquad\qquad\quad | \\
| \qquad\quad \text{CH}{-}\text{CH}_2{-}\text{CH}{-}\text{CH}_2 \;\; \text{CH}{-}\text{CH}_2{-} \\
{-}\text{CH}{-}\text{CH}_2{-} \;\; | \qquad\qquad\qquad | \\
\qquad\qquad\; \text{O}{-}\text{CO}{-}\text{CH}_3 \qquad \text{O}{-}\text{CO}{-}\text{CH}_3 \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad x
\end{array}
$$

polyvinylchloride
acetate
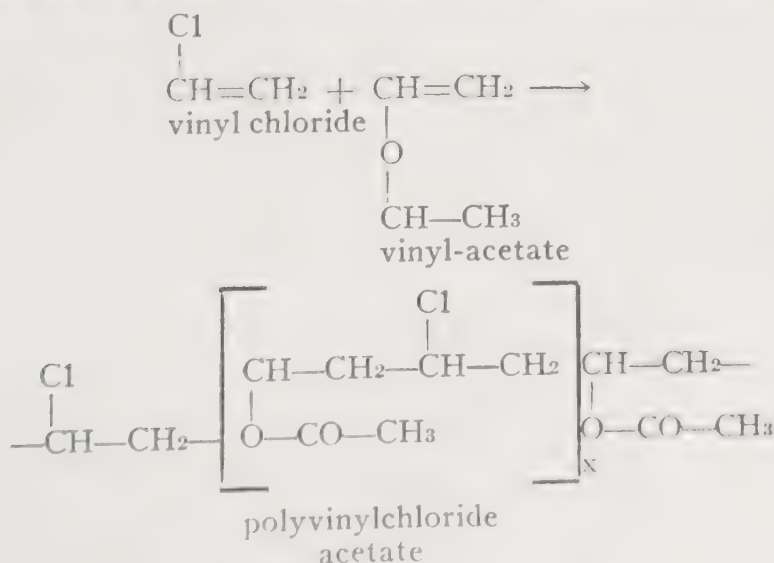
merisable alone to high molecular compounds by similar influences. The process of connection takes place somewhat according to the formula on page 51.

Naturally the sequence within these polymeric mixed products will not be exclusively regular and correspond only to the above formula. Molecules of the same class of substances will also polymerize partly with themselves and so may contribute to the formation of mixed mixed-polymerisates. These irregularities in combination will be especially great in the case of components with varyingly great capacity for polymerisation. In order to obtain here in spite of this the most uniform products possible, the reaction is controlled by continual addition of the partner most easily polymerisable.
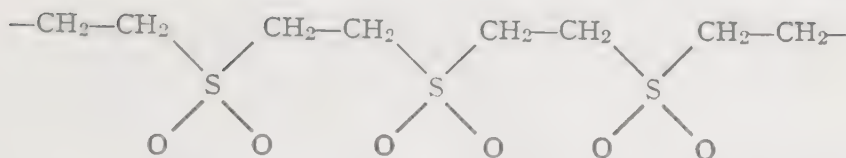
By **abnormal** mixed polymerisation, also called **hetero-polymerisation**[22]**)**, is usually understood the union of two structurally similar, but in capacity for polymerisation very different, molecules to a mixed polymerisate. For example, it is possible to unite a component not polymerisable in itself in a mixture with another polymerisable to a high polymeric, uniform product. In this connection it is worthy of note that not all non-saturated compounds are suited to hetero-polymerisation. The substituents in the acetylene union strongly influence the processes that take place. It is a conspicuous fact that precisely those substances are inclined to hetero-polymerisation which are less suitable for isopolymerisation[23]). Such non-saturated compounds which themselves do not polymerise are for ex. crotonic acid, maleic acid or their derivatives. For example, with maleic anhydride styrol forms a mixed polymerisate of the following structure:

$$
\begin{array}{c}
C_6H_5 \\
| \\
- CH - CH_2 - \quad CH - CH - \\
\qquad\qquad\quad | \qquad | \\
\qquad\quad O{=}C \quad C{=}O \\
\qquad\qquad \diagdown \quad \diagup \\
\qquad\qquad\quad O
\end{array}
$$

With the hetero-polymeres may also be counted those polymeric compounds arising from ethylene or butadien hydrocarbons (for ex. isoprene) under the influence of sulphur dioxide. These polymeric sulfones are extraordinarily high molecular[24]).

An analogous distinction can be made in the case of

$$-CH_2-CH_2 \diagdown \underset{O \diagup \diagdown O}{S} \diagup CH_2-CH_2 \diagdown \underset{O \diagup \diagdown O}{S} \diagup CH_2-CH_2 \diagdown \underset{O \diagup \diagdown O}{S} \diagup CH_2-CH_2-$$

processes of polycondensation between **isopolycondensation** (for ex. condensation of oxyacids with one another according to **Carothers**) and **hetero-polycondensation** (for ex. condensation of formaldehyde with phenol).

3. Dehydro- and Hydro polymerisation[25]).

Under the influence of many chemical substances, as for ex. sulphuric acid, aluminum chloride, or zinc chloride on saturated or non-saturated aliphatic or aromatic hydrocarbons, such as petroleum, cracked benzin, tar oil in a given case by heating or other influences, several reactions occur simultaneously[26]). Often a conversion is observed of the compounds in question by dehydrogenation, polymerisation, and finally by hydrogenation. These processes which finally lead to the formation of resins or substances similar to asphalt, often take place in distillation, even in the absence of oxygen. These processes are unclear in detail and very little investigated as yet.

The resinous substances formed during these processes of polymerisation are probably not true polymeres of olefins originally present, but the result of cleavage and dehydrogenation processes and of an ensuing polymerisation. Thereby oxygen will naturally strengthen a dehydrogenation begun possibly by thermic influences and so contribute to increased polymerisation. Technology is already making use of this knowledge.

It is known that low molecular saturated hydrocarbons disintegrate under strong heat according to the pressure partly into non-saturated low molecular hydrocarbons and hydrogen. In the thermic disintegration of petroleum under suitable conditions non-saturated hydrocarbons, mono-olefins, and di-olefins are formed. These non-saturated parts polymerise. For example, by heating ethane, ethylene and hydrogen are formed by primary disintegration[27]).

$$C_2H_6 \xrightarrow{600° C} = C_2H_4 + H_2.$$

But reactions may also take place leading to the formation of polymerisation products according to $2 C_2H_4 =$

$(C_2H_4)_2$ or $C_4H_8 + C_2H_4 = C_6H_{12}$ or hydrogenated products. From methane and ethane resins are supposed to be formed containing polybutadien and polyindene. In general in such resinifying processes not ethylene but higher moleculars are chiefly concerned, since it is well known that ethylene polymerises with but comparative ease and only by special processes.

Regarding the formation of these various dehydro- and hydro-polymerisation products from low molecular organic compounds, as remarked at the beginning, perhaps the following ideas can now be entertained. By the migration of hydrogen a part of the substance in question is **dehydrogenized.** By the cleavage of hydrogen, further non-saturated groups arise, not originally present, which give occasion for polymerisation. Under the influence of catalysts present and by heating, polymeres are formed which may be either non-saturated (dehydro-polymeres) or products hydrogenized later by hydrogen. These dehydrogenation and hydrogenation reactions have been studied in low molecular compounds, but thus far have met with little success in the case of high molecular products. The processes of polymerisation often lead not to a separation of resinous parts but only to a thickening of the original raw material. The polymeric substances formed in distillation represent today generally very undesired by-products. If, however, cheap low molecular hydrocarbons could be successfully converted by polymerisation into high molecular, clear, elastic, hard, and film-forming products (as others for instance are formed indirectly by ways of chlorinated products), then these processes might be of use.

IV. INFLUENCE OF THE CONSTITUTION ON THE CAPACITY FOR POLYMERISATION OF LOW MOLECULAR COMPOUNDS[28])

It was shown that polymerisations of low molecular compounds are conditioned by their chemical constitution[29]). In that connection it was pointed out that these components of higher molecular substances must somehow or other be non-saturated, so that in them $C = C$ or $C = O$ or $C = N$ — unions must be present in chain- or ring-shaped formation. The polymerisation rests on a compensation of valence or tension. According to previous views, the **arrangement of double unions** and the presence and **position of substituents** is essential for the course of the molecule enlargement in monomeric mole-

rules, while outward influences are also significant for the rapidity of these reactions. In the following an attempt is made to summarize the known facts. Here by substances polymerisable "easily" or "with difficulty" are to be understood such substances as can be polymerized easily or with difficulty under generally customary influences. Ordinarily there is a simultaneous connection between capacity for polymerisation and the extent of polymerisation in a properly conducted reaction. The extent of a polymerisation, however, depends considerably on outer conditions, and is not treated especially here.

From the many single observations noted in the literature, a clear idea can now be obtained regarding these processes of such importance to technology. Unanimous observations are present regarding the most essential points and the most important questions, even if it is often difficult to evaluate correctly the many results of experiments obtained under changing test conditions, in which observations the differences in the degree of purity of the substances used and resulting play a part. Nevertheless even under unfavorable conditions conclusions can be reached from these observations regarding the structure of high polymeres and the course of polymerisation.

The regularities found show that it depends on **definite systems or groups** in low molecular compounds, which filled with hydrogen atoms, are themselves polymerisable compounds or can induce capacity for polymerisation in the structure of a larger molecule. These observations are of importance in so far as they show the ways in which a non-polymerisable molecule can be changed into a polymerisable molecule. In table 3 are cited connections between the structure of important non-saturated groups, present in low molecular compounds, especially with reference to the kind and number of the double unions or ringforms present, their arrangement with regard to each other and of the resulting capacity for polymerisation. From general organic chemistry it is known that in many reactions and for many physical properties precisely the presence of such non-saturated groups of molecules or systems is of decisive significance. Examples of important non-saturated systems are the so-called **simple carbon double union** or **ethylene union**, the **3-fold carbon union** or acetylene union, also **coordinate, cumulative or isolated double unions,** finally **double unions between carbon and other**

Table 3. Capacity for polymerisation of various low mole[c

Group	Characteristic	Present for ex. Formula
—HC=CH—	carbon- c a r b o n - doubl. union (ethylene union)	$H_2C = CH_2$
		$H_2C = CH—R$
		$H_2C = CH — C_6H$
		$H_2C = CH—Cl$
$= C = O$	carbon - oxygen d o u b l e union (carbonyl union	$H_2C = O$
		$CH_3—CH{=}O$
		$C_6H_5—CH{=}O$
		$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\big\rangle\ C = O$
		$Cl_2—C{=}O$
$= C = N —$	carbon nitr. double union	$H_2C{=}NOH$
$— CH_2 —$	methylene group	radicals pres.
$= C = S$	carbon sulphur doubl. union (thionyl comp'd)	$H_2C{=}S$
$= C\!-\!\!-\!C =$ with O bridge	ethyleneoxide union	$H_2C{=}CH_2$ with O bridge
$\text{---} C \equiv C \text{---}$	carb.-carbon 3-fold union (acetylene comp'd.)	$HC{\equiv}CH$
$C \equiv N$	carbon nitrog. 3 fold union (nitryl union)	$H_2C—C{\equiv}N$

omp'ds. dependent on non-saturated groups.

Name	Poly- merizes	Poss. Structure of polymeric products
ethylene	gt. diff.	$- (CH_2 - CH_2)_x$.
olefin	difficult	$- CH_2 - CH - \left(CH_2 - CH \right)_x - CH_2 - CH -$ $\qquad\quad\vert \qquad\qquad\vert \qquad\qquad\qquad\vert$ $\qquad\quad R \qquad\qquad R \qquad\qquad\quad R$
styrol	easily	$- CH_2 - CH - \left(CH_2 - CH \right)_x - CH_2 - CH -$ $\qquad\quad\vert \qquad\qquad\vert \qquad\qquad\qquad\vert$ $\qquad\quad C_6H_5 \qquad\quad C_6H_5 \qquad\qquad C_6H_5$
vinyl- chloride	very easily	$- CH_2 - CH - \left(CH_2 - CH \right)_x - CH_2 - CH -$ $\qquad\quad\vert \qquad\qquad\vert \qquad\qquad\qquad\vert$ $\qquad\quad Cl \qquad\qquad Cl \qquad\qquad\quad Cl$
formalde- hyde	exceed. easy	$- CH_2 - O - \left(CH_2 - O \right)_x - CH_2 - O -$
acetalde- hyde	easily	$- CH - O - \left(CH - O \right)_x - CH - O -$ $\quad\vert \qquad\qquad\vert \qquad\qquad\quad\vert$ $\quad CH_3 \qquad\quad CH_3 \qquad\qquad CH_3$
benzal- dehyde	not	
ketone (acetone)	not	
halogen ketone phosgen	not	
formalde- hydeoxim. isonitrile	easily	$- CH_2 - N - \left(CH_2 - N \right)_x - CH_2 - N -$ $\qquad\quad\vert \qquad\qquad\vert \qquad\qquad\qquad\vert$ $\qquad\quad OH \qquad\qquad OH \qquad\qquad\quad OH$
n cracking	very easily	polymeric hydrocarbons
thiofor- maldehyde	easily	$\cdots CH_2 - S - \left(CH_2 - S \right)_x - CH_2 - S -$
ethylene oxide	easily	$- CH_2 - CH_2 - O - \left(CH_2 - CH_2 - O \right)_x - CH_2 -$)
acetylene	easily	cuprene; ring formation; chain polymeres.
yanimide	easily	ring formation

Capacity for polymerisation of various low molecular comp'd

Group	Characteristic	Presence Formula
$-\overset{..}{C}=\overset{..}{C}-\overset{..}{C}=\overset{..}{C}-$	coordinate carbon - carbon double bonds	$H_2C = CH — CH = CH_2$
		$H_2C = C — CH = CH_2$ $\quad\quad\quad\; \vert$ $\quad\quad\quad CH_2$ $CH————CH$ $\Vert \quad\quad\quad\quad \vert$ $CH_{} \quad\quad CH$ $\quad CH_2$
		$H_2C = C — CH = CH_2$ $CH \quad\quad \vert$ $\quad\quad\quad Cl$ $CH — CH = CH — CH_2$
$-\overset{..}{C}=\overset{..}{C}-\overset{..}{C}=O$	coordinate carbon-oxy gen-double bonds	$H_2C = CH — C = O$ $\quad\quad\quad\quad \vert$ $\quad\quad\quad\quad H$
		$H_2C = CH — C — CH_2$ $\quad\quad\quad\quad \Vert$ $\quad\quad\quad\quad O$
$--C — C--$ $\quad\; \Vert \;\;\; \Vert$ $\quad\; O \;\; O$	coordinate - oxygen — oxygen double bonds	$H_3C — C — C — H$ $\quad\quad \Vert \;\;\; \Vert$ $\quad\quad O \;\; O$
$--\overset{..}{C}=\overset{..}{C}-C\equiv N$	coord. carbon - carbon - nitrogen double bonds	$H_2C = CH — C \equiv N$
$--\overset{..}{C}=\overset{..}{C}-C\equiv C---$	coord. carbon - carbon - double - 3 fold bonds	$H_2C = CH — C \equiv CH$
$--C\equiv C-C\equiv C---$	coord. carbon - carbon - 3 fold bonds.	$HC \equiv C — C \equiv CH$
$--\overset{..}{C}=C=C--$	cumulative carbon - carbon-double bonds.	$CH_3— CH = C = CH_2$
$--\overset{..}{C}=C=O$	cumulative carbon - carbon - oxygen - double bonds	CH_3 $\quad\quad \diagdown C = C = O$ $CH_3 \diagup$
$O = C = O$	cumulative carbon - oxygen-double bonds.	$O = C = O$
$--C=C=N--$	cumulative carbon nit- rogen double bonds.	CH_3 $\quad\quad \diagdown C = C = NR$ $CH_3 \diagup$

dependent on non-saturated groups.

for ex. Name	Polymerized	Possible Structure of polymeric products
butadien	very easily	$- CH_2 - \left(CH_2 - CH = CH - CH_2 \right)_x - CH_2 -$
isoprene	very easily	$- CH_2 - \left(\underset{\underset{CH_3}{\vert}}{CH_2 - C} = CH - CH_3 \right)_x - CH_2 -$
cycl. diole-fins (cyclo-pentadien)	easily	$- CH - CH = CH - CH - \left(CH - CH = CH - CH \right)_x - CH -$ with CH_2 bridges
2-chlor-butadien	exceed-ingly easy	$- CH_2 - \left(\underset{\underset{Cl}{\vert}}{CH_2 - C} = CH - CH_3 \right)_x - CH_2 -$
propenyl-benzol	easily	$- CH_2 - \left(\underset{\underset{C_6H_5}{\vert}}{CH} - CH_2 - CH_2 \right)_x - \underset{\underset{C_6H_5}{\vert}}{CH} - CH_2 -$
Acrolein	very easily	$- CH_2 - \underset{\underset{CHO}{\vert}}{CH} - \left(\underset{\underset{CHO}{\vert}}{CH_2 - CH} \right)_x - CH_2 -$
methyl-vinyl-ketone	easily	$- CH - CH_2 - \left(CH - CH_2 \right)_x - CH -$ with $C - CH_3$, $\overset{\Vert}{O}$ groups
methyl-glyoxal	easily	$- O - CH - \left(O - CH \right)_x - O -$ with $CO - CH_3$ groups
vinyl cyanide	easily	$- CH_2 - \left(\underset{\underset{CN}{\vert}}{CH} - CH_2 \right)_x - \underset{\underset{CN}{\vert}}{CH} - CH_2 -$
vinylace-tylene	easily	$- CH - CH - \left(C = CH \right)_x - C \equiv C -$ with $CH_2 - CH_2$, $CH_2 - CH$ groups
diacetylene	easily	Constitution unknown; disintegrates
all hydro-carbons (methyl-allenes)	with difficulty	Constitution unknown
ketenes (dimethyl ketenes)	easily	$- \underset{\overset{\Vert}{O}}{C} - \left(\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - \underset{\overset{\Vert}{O}}{C} \right)_x - \underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - \underset{\overset{\Vert}{O}}{C} - :$ ring formation
carbon dioxide	not	$C - \left(\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - C \right)_x - \underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - C - :$ ring formation
ketimine	easily	with NR ... NR groups

Capacity for polymerisation of various low molecular comp'ds.

Group	Characteristic	Present Formula
$\cdots\overset{\cdots}{C}=\overset{\cdots}{C}-\overset{\cdots}{C}-\overset{\cdots}{C}=\overset{\cdots}{C}\cdots$	Isolated carbon - carbon double bonds	$\overset{CH}{\bigcirc}CH-CH_2-CH=CH_2$
$-\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdots}{C}-\overset{\cdots}{C}-\overset{\cdot}{C}=\overset{\cdot}{C}\cdots$		$CH_2=CH-CH_2-CH_2-CH=CH_2$
$\cdots\overset{\cdot}{C}=\overset{\cdot}{C}-O-\overset{\cdot}{C}=\overset{\cdot}{C}\cdots$		$H_2C=CH-O-CH=CH_2$
$\cdots\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdots}{C}-C=O$	Isolated carbon - carbon - oxygen double bonds	$CH_2=CH-CH_2-\underset{CH_3}{C}=O$
$\overset{\cdot}{C}=\overset{\cdot}{C}-O-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-O-\overset{\cdot}{C}=\overset{\cdot}{C}\cdots$		$H_2C=CH-O-C=O$ $H_2C=CH-O-\underset{}{C}=O$
$\cdots\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdot}{C}=\overset{\cdot}{C}\cdots$	Manifold coordinate carbon - carbon double bonds	$CH_2=CH-CH=CH-CH=CH_2$
$-\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdot}{C}\equiv\overset{\cdot}{C}\cdots$	Manifold coord. carbon-carbon-double and 3 fold bonds	$CH_2=CH-CH=CH-C\equiv CH$
$-\overset{\cdot}{C}=\overset{\cdot}{C}-C\equiv C-\overset{\cdot}{C}=\overset{\cdot}{C}-$		$CH_2=CH-C\equiv C-CH=CH_2$
$-C=C-C\equiv C-C\equiv C-C=C\cdots$		$CH_2=CH-C\equiv C-C\equiv C-C=CH_2$
$\cdots C=C-C=C-C=C-C=C\cdots$		$\overset{CH\diagdown}{\underset{CH}{\overset{CH}{\mid}}}\underset{CH\diagup}{\overset{}{\parallel}}\begin{matrix}-CH=CH_2\\-CH=CH_2\end{matrix}$
$\cdots\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdot}{C}=\overset{\cdot}{C}-\overset{\cdot}{C}=O$	Manifold coord. carbon-carbon-oxygen-double bonds.	$CH_3-CH=CH-CH=CH-C=O$ $\underset{CH_3}{\mid}$
$C=C-C=C-C-C=C-C=C\cdots$ $\underset{\overset{\|}{O}}{}$		$\underset{C_6H_5}{\overset{CH:CH-CH:CH-C-CH:CH-CH:CH}{\mid}}\overset{}{\underset{O}{}}\underset{C_6H_5}{\mid}$
$\cdots\overset{\cdot}{C}=\overset{\cdot}{C}-\underset{\overset{\|}{O}}{C}-\overset{\cdot}{C}=\overset{\cdot}{C}\cdots$		$H_2C=CH-\underset{\overset{\|}{O}}{C}-CH=CH_2$
$\cdots\overset{\cdot}{C}=\overset{\cdot}{C}-\underset{\overset{\|}{O}}{C}-C\equiv N$	Manifold coord. carbon-carbon-oxygen-nitrogen bonds.	$H_2C=CH-\underset{\overset{\|}{O}}{C}-C\equiv N$

dependent on non-saturated groups.

for ex. Name	Polymerized	Possible structure of polymeric products
Allylbenzol	with difficulty; or not	
Diallyl	with difficulty; or not	
Divinyl-ether	with diff. or easily in mixed poly-merisation	
vinyl-acetone	not	
oxalacid-divinyl-ester	with diff. or easily in mixed polymerisa-tion	
Hexatrien	easily	constitution unknown; (or ring formation)
Butadienyl-acetylene	easily	constitution unknown; disintegrates
Divinyl-acetylene	easily	$- CH - C \equiv C - CH -$ $\Big(CH_2$ $CH_2 \Big) - CH -$ $- CH_2$ $CH_2 - \Big(CH - C = C - CH \Big)_x CH_2$
Divinyl-diacetylene diacetylene	very easily	constitution unknown; disintegrates
Divinyl-benzol	very easily	$- CH - CH_2 -$ $\Big/ CH - CH_2 \Big\backslash$ $- CH - CH_2 -$ C_6H_4 C_6H_4 C_6H_4 $- CH - CH_2 -$ $\Big\backslash CH - CH_2 \Big/_x$ $CH - CH_2 -$
sorbicacid-methyl-ketone	easily	constitution unknown
diaiamylide acetone	easily	constitution unknown
divinyl-ketone	easily	$- CH - CH_2 -$ $\Big/ CH - CH_2 \Big\backslash$ $- CH - CH_2$ CO CO $- CO$ $- CH - CH_2 -$ $\Big\backslash CH - CH_2 \Big/$ $- CH - CH_2$ (x)
acrylic acid nitrile	espec. in mixed polymerisa-tion	$- CH_2 - CH -$ $\Big/ CH_2 - CH - \Big\backslash$ $CH_2 - CH$ CO CO CO CN $\Big(CN \Big)_x$ CN

atoms, for ex. oxygen or nitrogen. It is especially significant that not only the carbon chain but also a mixed structure often gives rise to similar conditions of reaction. The examples cited for the molecule groups in question in various compounds are those that have been used in great part for technological purposes. No attention will here be paid to the circumstances and conditions under which polymerisation leads to high polymeric products. The connections between the constitution of organic compounds and the capacity for polymerisation as well as frequently to the so-called formation of resins has led to the concepts expounded by Staudinger, Scheiber, Scheifele, Herzog and Kreidl, Eibner, Wolff, and others.

From the great number of the polymerisable compounds here selected and cited, there clearly results a certain "pleasure in conversion" of many monomeric molecules. These tensions are especially great in the compounds with **coordinate double bonds** and in those which have been further stimulated by suitable substition. We will later consider these further relationships further.

The excitability of the **ethylene combination** is shown in ethylene itself, even though weakly. It is itself polymerisable but only under very definite circumstances and leads then to oily products of not very high molecular weight. By substitution of hydrogen atoms the capacity for reaction in this case is nevertheless considerably increased, and the capacity for polymerisation becomes greater within certain limits, which is otherwise not the case, as usually low molecular substances possess the greatest capacity for polymerisation. Propyls and iso-butyls are according to this easily polymerisable. For example liquid isobutyl is polymerized by the introduction of boric fluoride at ca.—70° in the presence of solid carbon dioxide to a high polymeric, exceedingly elastic gum-like product. But if the hydrocarbon chain becomes longer, the products again become capable of reaction.

In the case of compounds with a **carbonyl double bond** ($C{=}O$), normal relations are present. Here the simplest product, formaldehyde, is most easily polymerisable. Acetaldehyde already possesses a significantly weaker capacity for reaction, which ceases entirely in the higher homologues. Analogous is the behavior of products with a carbon-nitrogen or a carbon-sulphur double bond.

An interesting reaction, similar to the polymerisation

of ethylene, is present in the so-called **methylene poly-merisation** which occurs for example in products which form or possess free methylene radicals. For example non-saturated radicals arise in cracking or there is formed from benzyl chloride by separation of hydro-chloric acid C_6H_5—$CH=$, which changes by polymeric processes entering at once into higher molecular sub-stances of the following structure:

$$-CH_2-C_6H_4-CH_2-[C_6H_4-CH_2]x-C_6H_4-.$$

But if the separation of hydrochloric acid is taken into consideration, this reaction can also be regarded as poly-condensation. The easy capacity for polymerisation of **closed ring or intrinsic anhydrides,** such as ethylene oxide for ex., induced by catalysts, probably rests chiefly on the tendency of these alkylene oxides to offer a certain resistance to their ring-formation. The mani-fold conversions possible with these substances further show—although the bodies are closed rings and possess no double bonds—nevertheless a relatively strong non-saturated tendency capable of leading by active poly-merisation to comparatively high polymeres. If this re-active conduct of the low alkylene oxides is compared with the properties of their higher ring-homologues, for ex. with tri-, tetra-, and penta-methylene oxide, it is seen that they are formed with far greater ease, but that the reopening of their ring and the accompanying polymerisation becomes much more difficult or even impossible. Analogous is the fact that benzol is constant despite its coordinate double bonds, while non-saturated aliphatic hydrocarbons on the other hand are poly-merisable.

Of special significance for the modern acetylene chemistry is the **action of the acetylene group in excit-ing polymerisation.** By employing the capacity for poly-merisation of the basic substance acetylene and direction of the reaction, the chemistry of the acetylene com-pounds experienced in recent years a significant impetus. Formerly only the high molecular products were known present in **cuprene,** a cork-like mass, and those express-ing the capacity for polymerisation of acetylene. Only by clever direction by means of complex heavy metal catalysts, such as were utilized by **Niewland,** was a moderated polymerisation successful leading to low polymeric, still non-saturated products, which can be further polymerised, since they contain typical non-saturated polymerisable groups of the acetylene series.

Here the higher homologues are less easily polymerisable, for ex. dimethyl acetylene or phenyl acetylene polymerize with difficulty.

The polymerisation of **compounds with two equal or different non-saturated double bonds** possess especial theoretical, practical and economic interest. Three kinds are here distinguished, according to their momentary position: coordinate, cumulative, and isolated double bonds. A system of **coordinate double bonds** is usually shown in different directions as quite especially reactive. The compounds of this group tend strongly to polymerisation and are essentially more reactive than those with isolated or cumulative double bonds or with simple acetylene combination. Thus butadien changes much more easily into a polymere than ethylene or ethyl ethylene. Therefore the products are of great technical significance because they usually yield caoutchouc-like products. Thus the excellent German synthetic caoutchouc "Buna" is a polymerisate of butadien, the American synthetic caoutchou "neoprene" or "duprene" is a polymeric chlorobutadien product. In the consideration of these groups influencing polymerisation, it is clearly recognized that not only coordinate pure carbon double bonds are distinguished by especial reactive capacity, but that also coordinate double bonds with other atoms, thus with the $C=O$- or $C\equiv N$—group, show very similar conduct. Thus acrolein for ex. is polymerized through its cordinated double bonds far more easily than propionic aldehyde, which has only one $C=O$- double bond; vinyl cyanide behaves similarly in comparison to ethyl cyanide. Without depreciating the influence on the ethylene combination of a negative substituent strengthening polymerisation still compounds are found also in vinyl-methyl-ketone $CH_2=CH—\underset{\underset{O}{\|}}{C}—CH_3$ as well as isopro-

penyl- methyl-ketone $CH_2=\underset{\underset{CH_3}{|}}{C}—\underset{\underset{CH_3}{|}}{C}=O$ which do not
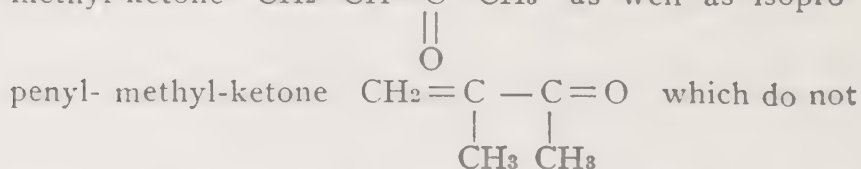
decisively contain such substituents and are still very easily polymerized. Thereby the presence in the previously named compounds of a definite non-saturated group can be made responsible for the polymerisation, since otherwise ethyl-methyl-ketone and propyl-methyl-ketone do not react. This is also in accord with the fact that compounds with an ethylene double bond are easily

polymerized when a further double bond enters the ethylene combination in a coordinate position.

Increased scientific interest is also claimed by the so-called **cumulative double bond** or allene groups, most widely disseminated in various hydrocarbons but especially in the ketenes[30]). These substances possess partly very active capacity for polymerisation, but form no very high molecular products of practical use. Between hydrocarbons and acetylene homologues there are many transitions. The previous ideas about the structure of the polymeres formed from them are still very dim[31]). The polymerisation of ketenes or their numerous homologues possible has not yet taken place in the technical field.

Compounds with **isolated double bonds** show essentially the behavior of the simple olefines, but in most cases they have a very slight capacity for polymerisation. While for ex. propenyl-benzol is polymerized with comparative ease, allyl-benzol changes to a polymere with difficulty and often not at all[32]). If in both products the group partly lying in the benzol ring is considered, in one case coordinated, and in the other isolated double bonds are recognized,
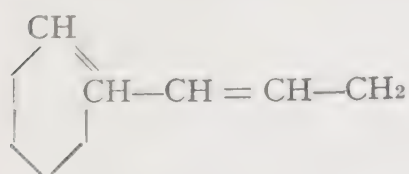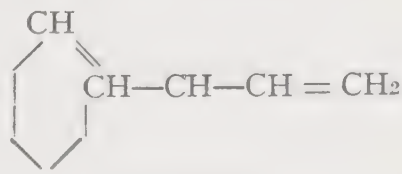
propenylbenzol   allylbenzol

which determine the different behavior of these basic substances as well as that of their corresponding derivatives like isosafrole, and safrole, isoeugenol and eugenol, anethole and estragole. In short, there is present in styrol or indene a coordinate non-saturated system when this is represented as passing into the benzol ring.
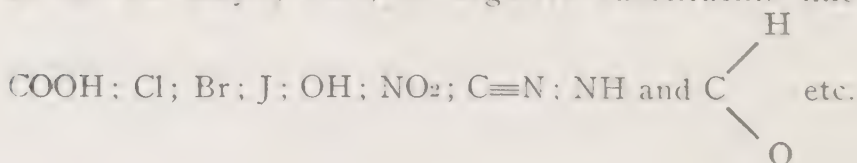
Similarly compounds with three or more coordinate double bonds show very great capacity for polymerisation, which for ex. in the case of a natural product, wood oil, in contrast to linseed oil, is essentially increased by the presence of such groups in its acid residues[33]).

An interesting accumulation of double coordinate bonds is found in the molecule of divinyl-benzol, which is very easily polymerized.

V. THE INFLUENCE OF SUBSTITUENTS ON THE CAPACITY FOR POLYMERISATION OF LOW MOLECULAR COMPOUNDS

In very many compounds the capacity for polymerisation of the basic substance in question is essentially increased by definite substituents and by their corresponding position. The new compound then polymerises easily or with difficulty or not at all. Frequent reference has already been made to these important facts the knowledge of which makes it possible to perform the synthesis according to the properties expected of the polymeric substances. Technology has already made use of these possibilities in the production of many synthetic high polymeres. If these interesting questions are considered more closely, it is often difficult to decide whether the substituents or the resulting structure of the compounds in question, or of the previously named groups are alone decisive for the capacity for polymerisation. This is true, for ex. for the case of the addition of a non-saturated substituent to the ethylene compound, whereby a coordinate non-saturated system results. It has not always been easy to determine fundamentally how to dispose of these differences in this summary for the sake of clearness.

The influence of a substituent according to kind and position on polymerisation of one or several non-saturated compounds can be best understood by making use of the supposition regarding the capacity for polymerisation of ethylene derivatives put forth by **Michael**[34]). According to that the polymerisation of ethylene derivatives is dependent on a polar opposition of the two atoms of ethylene carbon, and moreover there exists in a non-saturated substance less inclination to polymerisation if this polarity is slight, while compounds with greater polarity are easily polymerized[35]). Of prime importance in favor of this is the fact that the symmetrically substituted ethylenes chiefly possess a decided inclination for polymerisation. Thus the asymmetric dichlor-ethylene is very easily polymerized in contrast to the symmetrical. Further, crotonic acid ester is more constant than methyl-acrylic acid ester. Substituents are considered such as those having varying decisive character, as for ex. alkyls, HN_2, or negative substituents like

$$COOH; Cl; Br; J; OH; NO_2; C{\equiv}N; NH \text{ and } C\begin{smallmatrix} H \\ \diagup \\ \diagdown \\ O \end{smallmatrix} \text{ etc.}$$

If such a negative substituent enters a carbon atom, the latter receives a positive character. The added substance, however, will have a relatively negative nature compared with the first. In the case of positive substituents it is exactly reversed. Thereby correspondingly great attractive powers will appear from molecule to molecule, finding expression in our case as polymerisation. Such influences of changing "induced polarity" are known in organic chemistry and are found for ex. also in the case of making an aromatic bound halogen mobile by negative substituents in ortho- or para-nitrochlorbenzol. Various substituents also influence the capacity for polymerisation when they do not enter directly into the double bond but into a lateral group (varying capacity for polymerisation of various derivatives of styrol).

Ethylene and acetylene, compounds which are relatively difficult to polymerise, are converted into substances very easily polymerisable by the entrance of such positive and chiefly negative substituents. Thus vinyl chloride, vinyl acetate, acrylic acid ester, acetylene halides are very easily polymerized and form partly high molecular polymeric products (Cf. Table IV). Easily polymerisable butadien is also further activated by the entrance of a substituent, especially by chlorine. On the other hand compounds with a carbonyl double bond experience a lessening of inclination for polymerisation towards the ethylene compound (benzoic aldehyde, phosgene) by means of certain negative substituents such as phenyl, hydroxide and, above all, chlorine.

Table 4. Influence of Substituents on Capacity for
acetylene and

| Basic Subst. | | Compound | |
Formula	Name	Formula	Name
$H_2 = CH_2$	ethylene gt. diff.	$C_6H_5-CH=CH_2$	styrol
		$CH_3-CH=CH_2$	propylene
		$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> C = CH_2$	dimethylethylene
		$CH_3-O-CH=CH_2$	vinylether
		$R_2N-CH=CH_2$	vinylamine
		$NC-CH=CH_2$	vinylcyanide
		$Cl-CH=CH_2$	vinylchloride
		$Cl_2-CH=CH_2$	dichlorethylene
		$CH_3-CO-O-CH=CH_2$	vinylacetate
		$HOOC-CH=CH_2$	acrylicacid
		$CH_3-O-CO-CH=CH_2$	acrylicester
		$O=C=CR_2$	ketene

Polymerisation of some important ethylene, butadien, carbonyl comp'ds.

Polymerizes	Possible Structure of Polymeric Products
gt. diff.	$-(CH_2-CH_2)_{\overline{x}}-$; ring formation
easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, C_6H_5 \qquad\quad C_6H_5 \qquad\quad C_6H_5$
diff.	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, CH_3 \qquad\quad CH_3 \qquad\quad CH_3$
easily	$\quad\;\; CH_3 \qquad\quad CH_3 \qquad\quad CH_3$ $-C-CH_2-\left(C-CH_2\right)_x-C-CH_2-$ $\quad\,\, CH_3 \qquad\quad CH_3 \qquad\quad CH_3$
easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, OCH_3 \qquad\quad OCH_3 \qquad\quad OCH_3$
easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, NR_2 \qquad\quad NR_2 \qquad\quad NR_2$
easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, CN \qquad\quad CN \qquad\quad CN$
very easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, Cl \qquad\quad Cl \qquad\quad Cl$
diff.	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, Cl_2 \qquad\quad Cl_2 \qquad\quad Cl$
very easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2$ $\quad\,\, O-COCH_3 \;\; O-COCH_3 \;\; O-COCH_3$
very easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, COOH \qquad\quad COOH \qquad\quad COOH$
very easily	$-CH-CH_2-\left(CH-CH_2\right)_x-CH-CH_2-$ $\quad\,\, CO-O-R \;\; CO-O-R \;\; CO-O-R$
easily	constitution unknown

Influence of Substituents on Capacity for Polymerisation carbonyl

Basic Subst.		Compound	
Formula	Name	Formula	Name
CH≡CH	ace-tylene	$CH_3 - C \equiv C - CH_3$	Dimethylacetylene
		$C_6H_5 - C \equiv CH$	Phenylactylene
		$HOOC - C \equiv CH$	Propionic acid
		$Br - C \equiv CH$	Bromacetylene
$CH_2=CH-$ $CH=CH_2$	bu-tadien	$CH_2= C - CH = CH_2$ $\quad\quad\;\; | $ $\quad\quad CH_3$	Isoprene
		$CH_2= C - C = CH_2$ $\quad\quad \| \quad\; \|$ $\quad\; CH_3\; CH_3$	2-3-Dimethyl-butadien
		$CH_3 - CH = C - CH = CH_2$ $\quad\quad\quad\quad\quad \|$ $\quad\quad\quad\quad CH_3$	1-2-Dimethyl-butadien
		$CH_2= C - CH = CH_2$ $\quad\quad \|$ $\quad\; Cl$	2-Chlorbutadien (Chloropren)
		$CH_2= C - CH = CH_2$ $\quad\quad \|$ $\quad\; Br$	2-Brombutadien
		$CH_2= C - C = CH_2$ $\quad\quad \| \quad \|$ $\quad\; Cl \quad Cl$	2-3-Dichlorbutadien
$CH_8=O$	For-malde-hyde	$CH_3 - CH = O$	Acetaldehyde
		$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \Big\rangle C = O$	Acetone
		$C_6H_5 - CH = O$	Benzaldehyde
		$CH_2= CH - CH = O$	Acrolein
		$CH_3 - CO - CH = O$	Methylglyoxal
		$HOOC - CH = O$	Glyoxylacid
		$Cl_2 - C = O$	Phosgene
		$O = C = O$	Carbondioxide

oi some important ethylene, butadien, acetylene and comp'ds.

Polymerized	Poss. Structure of polymeric products
with diff.	cuprene; ring formation
very diff.	Constitution unknown
very diff.	Constitution unknown
very diff.	Constitution unknown
easily	Constitution unknown
easily	$-CH_2-(CH_2-CH=CH-CH_2)_{\overline{x}}-CH_2-CH=CH-CH_2-$
very easily	$-CH_2-\left(CH_2-\underset{\underset{CH_3}{\mid}}{C}=CH-CH_2\right)_x-CH_2-\underset{\underset{CH_3}{\mid}}{C}=CH-CH_2-$
very easily	$-CH_2-\left(CH_2-\underset{\underset{CH_3}{\mid}}{C}=\underset{\underset{CH_3}{\mid}}{C}-CH\right)_x-CH_2-\underset{\underset{CH_3}{\mid}}{C}=\underset{\underset{CH_3}{\mid}}{C}-CH_2-$
very easily	$-CH_2-\left(\underset{\underset{CH_3}{\mid}}{CH}-\underset{\underset{CH_3}{\mid}}{C}=CH-CH_2\right)_x-\underset{\underset{CH_3}{\mid}}{CH}-\underset{\underset{CH_3}{\mid}}{C}=CH-CH_2-$
ext. easily	$-CH_2-\left(CH_2-\underset{\underset{Cl}{\mid}}{C}=CH-CH_2\right)_x-CH_2-\underset{\underset{Cl}{\mid}}{C}=CH-CH_2-$
ext. easily	$-CH_2-\left(CH_2-\underset{\underset{Br}{\mid}}{C}=CH-CH_2\right)_x-CH_2-\underset{\underset{Br}{\mid}}{C}=CH-CH_2-$
ext. easily	$-CH_2-\left(CH_2-\underset{\underset{Cl}{\mid}}{C}=\underset{\underset{Cl}{\mid}}{C}-CH_2\right)_x-CH_2-\underset{\underset{Cl}{\mid}}{C}=\underset{\underset{Cl}{\mid}}{C}-CH_2-$
ext. easily	$-CH_2-O-(CH_2-O)_{\overline{x}}CH_2-O-$
easily	$-\underset{\underset{CH_3}{\mid}}{CH}-O-\left(\underset{\underset{CH_3}{\mid}}{CH}-O\right)_x-\underset{\underset{CH_3}{\mid}}{CH}-O-$
not	condensation
not	condensation
very easily	$-CH_2-\underset{\underset{CHO}{\mid}}{CH}-\left(CH_2-\underset{\underset{CHO}{\mid}}{CH}\right)-CH_2-\underset{\underset{CHO}{\mid}}{CH}-$
easily	$-\underset{\underset{COCH_3}{\mid}}{CH}-O-\left(\underset{\underset{COCH_3}{\mid}}{CH}-O\right)_x-\underset{\underset{COCH_3}{\mid}}{CH}-O-$
easily	Constitution unknown
not	————
not	————

Table 5. Capacity for Polymerisation of Various Compounds. With Coordinate Double Bonds

Basic Substance polymerized	substituents in basic substances in a-position polymerizes with diff. or not	substituent in basic substance in b-position polymerizes easily
CH2=CH—CH=CH2 butadien	CH=CH—CH=CH2 / Cl 1-chlorbutadien	CH2=C—CH=CH2 / Cl 2-chlorbut. (chloroprene)
	CH=CH—CH=CH2 / CH3 1-methylbutadien	CH2=C—CH=CH2 / CH3 2-methyl butadien (isoprene)
	CH=CH—CH=CH2 / C6H5 1-phenylbutadien	CH2=C—CH=CH2 / C6H5 2-phenylbutadien
CH2=CH—C=O / OH acrylic acid	CH=CH—C=O / CH3 ... OH crotonic acid	CH2=C—C=O / CH3 OH methacrylic acid
	CH=CH—C=O / C6H5 ... OH cinnamic acid	
	CH=CH—C=O / CH3 ... O-CH3 crotonic acid-methylester	CH2=C—C=O / CH3 O—CH3 methacrylic acid methyl ester
CH2=CH—C=O / H acrolein	CH=CH—C=O / CH3 ... H crotonaldehyde	CH2=C—C=O / CH3 H methacrylic aldehyde
	CH=CH—C=O / C6H5 ... H cinnamic aldehyde	
CH2=CH—C=O / CH3 vinylmethyl-ketone	CH=CH—C=O / CH3 ... CH3 ethylidene acetone	CH2=C—C=O / CH3 CH3 isopropenyl-Methyl ketone

It is interesting that if the polarity of a non-saturated system exceeds a definite degree, lessening of the capacity for polymerisation again occurs, or that the original effect can again be suspended by the entrance of a negative substituent into a positive group[36]). Similar relations occur when two negative substituents enter symmetrically into a non-saturated system, whereby reduction or complete stoppage of polymerisation occurs (sym-dichlor-ethylene). All these relations have been studied extensively in various derivatives of the ketene[37]).

From many examples drawn from organic chemistry, it is known that not only the kind of the substituents, but also their position play an important part and is of influence on the course of the reaction. Similar relations are also present in the processes of polymerisation. The influence of a different position of the same substituents on the capacity for polymerisation of low molecular compounds is most clearly shown in compounds with **coordinate double bonds,** especially in compounds with the vinyl group in a neighboring position to the non-saturated group. In all these products, such as butadiene, acrolein, acrylic acid, styrol, polymerisation is made essentially more difficult or even stopped by substitution in a neighboring position to the non-saturated group, that is 1- or a- position, while it is made considerably easier by the substitution in 2- or b- position[38]). These manifestations led precisely in technology, as mentioned, to unsuspected important results. Above all intermediate products have technical significance which have been obtained by treatment of acetylene polymeres like vinylacetylene with hydrochloric acid and polymerise easily and can be converted into high molecular products similar to gum[39]). Such a derivative of chlorbutadien with decided capacity for easy polymerisation forms high molecular neoprene Just so the b-methyl derivatives of acrylic acid or their esters have become important raw materials for synthetic high polymeres, whose chief representative is plexiglass. These monomeric products have by their corresponding substitution in contrast to their basic substances (for ex. crotonic acid) increased capacity for polymerisation, and their polymeres show physical properties in close connection with their structure. Various derivatives of styrol, such as oxy-, methyl-, ethoxy-styrol, have according to the position of the substituents in ortho-, para, or meta- position, varyingly great capacity for polymerisation, and moreover the para- or ortho-derivatives polymerise more easily. If the corres-

ponding substituents are too large or too heavy, the capacity for polymerisation is lowered despite favorable position (vinyl napthalene). In table 5 various compounds are cited side by side for survey[49]).

The scientific study of the chemistry of polymerisation has in any case brought clearness to this branch of organic chemistry, although we have not advanced to the point where the chemism of reactions is comprehended in all details. The technical supervision of these processes demands to be sure much experience, especially if it is desired always to obtain uniform products, which are superior to many natural products. The consideration of various view-points regarding the processes of polymerisation brings the recognition that not only technical processes and machines determine the desired physical properties and quality values of synthetic substances, but that precisely the knowledge of the structure and the capacity for reaction of low molecular organic compounds can contribute considerably to obtaining final products with definite desired properties.

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PRINCIPLES OF THE PROCESSES
OF POLYCONDENSATION

Insight into the chemism of macromolecular formation and the scientific investigations of "high moleculars" have lagged far behind compared with their practical application in industry; it had to be so of necessity because macromolecular chemistry saw itself face to face with tasks which could not be solved by means of classical chemistry. Works of recent years have cleared up many questions so that today the worker in and user of synthetic resins no longer needs to be satisfied with controlling outer manifestations and technical conditions of his procedure, but is also in the position of gaining a comprehension of the chemical processes lying at the foundation of his production.

From olden times natural products have been used as materials for most diverse purposes, whose chemical structure, according to our present conception, must be designated as "high molecular." Here belong the albumins of food, of animal skins, and of wool, the cellulose of vegetable fibres, the resins and caoutchouc of trees. All these products are even today of at least the same significance as they were centuries ago. The satisfaction by such natural products of all demands extends only to certain limits. Therefore the attempt was made to extend, if possible, the basic materials.

Chemical Change of Natural Substances

With the aid of chemical knowledge these natural substances were partly changed into new materials, which then very often exhibit completely new properties[2]). Thus there were produced by "rational syntheses" from cheap natural resins valuable gum lacs, from copals lacs, from linseed oil by the joint use of filling media linoleum, from cottons artificial silks, from caoutchouc gum of most diverse kinds and from casein hard products which have become of great economic significance as horn substitute[3]). The chemical reactions chiefly used in the conversion of natural substances are esterification, nitrification (cellulose acetate and cellulose nitrate), etherization, chlorination (chlorocaoutchouc), oxydation, acetification, and many others. With the increasing application of such improved raw materials, there was a greater proportional increase of claims made as regards quantity and proper-

ties which occasionally could no longer be filled in both directions.

Syntheses of High Molecular Substances

Hence significance was given to processes designated as "pure syntheses" which permit the composition of new high molecular substances from low molecular substances less capable of application. Among these are to be counted most important reactions in the field of high moleculars, namely **polymerisation** and **polycondensation.** As the methods of formation of high molecular compounds by polymerisation has previously been described, now these processes of production of high molecular substances designated as polycondensation are to be treated[4]). To give a real total survey of this field that has become almost impossible to summarize, is impossible here. Hence only such products of polycondensation, which as **pure** syntheses lead to production of use technologically, will be treated here.

The Nature of Condensation Reactions

As is known from general organic chemistry, condensation in the field of low moleculars form the means most in use for the synthetic acquisition of substances while the significance of polymerisations drops back strongly in that field[5]). To a certain extent they are the opposite of saponifications and are distinguished by the fact that according to formula from two molecules a chemically simple structure, such as water, hydrogen halide, ammonia, or hydrogen sulphide is separated while the rest of both molecules unite to form a product usually of higher molecular weight. The formulas of the new products of condensation represent either a chain or a ring. By the combination of the two original molecules arise C-C, C-O-, C-N, C-S- compounds, which are constant in the face of a repeated separation. Condensations take place in many cases without serious difficulties, while in other cases the reaction must be assisted by supplying heat or by the addition of catalytically effective substances. The united remainders of the molecules may be of considerable size; thus it has become possible in the field of albumin chemistry to obtain condensation products with a demonstrable molecular weight up to 5000[6]).

There are cases now in which condensation occurs somewhat too easily. Then substances are formed whose

molecular weights project almost or entirely into the field of high moleculars, which however by that very fact formerly gave the chemists little joy because they form the ill-famed "resinous and oily residues." There are two possibilities for the occurrence of such large complexes. First, the **remainders of the molecules** that unite mutually may already be very large; and second the molecule formed from the two remainders may have at its disposal a group capable of condensation which with another such a group of a second molecule from the reaction mixture concerned, enters again into condensation, whereby under circumstances a high molecular substance with another reactive group arises, which is again capable of condensation. Such **continuous condensations** are designated as **polycondensation.** They are of the greatest importance for the production of high molecular compounds, and on the basis of more recent knowledge it is to be assumed that even the high moleculars occurring in nature, such as albumin and cellulose, arise through polycondensation from small molecules with a comparatively simple structure. Therefore it is not to be wondered at that condensation reactions finally began to be conducted purposely so that the originally undesired high moleculars were produced.

Technical Exploitation

The first success was obtained by the technical exploitation and conduct of polycondensation, which occurs under the influence of formaldehyde, or its polymeres, on phenol. As this reaction which occurs so easily is controllable variously, the most manifold products or new raw materials, the **phenol resins,** were soon reached. The phenol resins therefore form the chronological start of the series of **synthetic substances won by purely synthetic means,** and in the course of time their significance has increased manifold. Since the value of these condensation processes has been recognized everywhere, there began a general search for easily obtainable, cheap substances suitable for polycondensation. Today a glance into the voluminous patent literature in this field that has developed in the last decades seems to indicate that all products coming in question have already been investigated in this regard. But it is also shown that of the many possibilities that have arisen, only very few could satisfy practical demands. But these few have found in proportion an exceedingly extensive application in

most diverse fields, and, **along with** the products of poly-
merisation which acquired technological interest only in
recent years, and natural substances, best fill their place
in modern economic life.

The greatest significance of the polycondensates rests
above all on the fact that very many occur both in a
fluid intermediate state and also in a solid final condition,
in which they become insoluble and infusible. Thereby
it is possible to pour polycondensates into moulds and
then convert them into hard products of most manifold
form, or to mix them with cheap filling media, and so
change them into hard, comparatively cheap objects that
resist breakage. Finally the fluid intermediate products
can be dissolved in suitable solvents and used then as
lacs which can become extraordinarily hard.

The products of polymerisation previously described
are on the other hand mostly fairly soft, partly gum-like
masses, becoming plastic in warmth and so satisfying
very different demands from those met by the products
of condensation.

Differences between Polymerisation
and Polycondensation

In considering the synthetic substances so valuable
for technology today, the first conspicuous fact is that
products produced by polymerisation especially are
slightly branched and are composed only of threadlike
molecules of considerable length. On the other hand
by the process of polycondensation it does not in general
amount to more than a medium degree of polymerisation
or polycondensation, in so far as there is a possibility of
forming chain-shaped molecules. But since good techni-
cal properties do not appear until the particles have
attained a certain size, technology makes use of the ori-
ginal products in producing by means of polycondensa-
tion, synthetic substances which possess more than two
reactive groups per molecule in order thus to have the
bases for forming high molecular compounds that are
strongly branched by means of three-dimensional conca-
tenation. Therefore it is not strange that such technically
valuable condensates with but few exceptions are not
composed of linear chain molecules like the products of
polymerisation. The reason for the slighter reactivity
in condensation reactions in the direction of chain forma-
tion rests on two completely distinguishable reactions.

The Mechanism of Reaction[7]).

Polymerisation is a chain reaction in the course of which molecules with free valences first appear which are spontaneously converted and linked into a chain[8]). If the conditions are favorably chosen, then the still free valences at the end of the growing chains are only very tardily saturated by for ex. final groups, migration of oxygen atoms, closure of the ring, accumulation of impurities and the like. In this way then extraordinarily long molecules arise. While these processes take place without loss of substance and presuppose only a definite non-saturated condition of the **monomeric molecules** entering into the reaction, polycondensation reactions can, as said, always take place when **molecules suited to a polymorphous conversion or condensation meet,** which therefore because of the groups contained in them possess the capacity of frequently entering new unions, and are furthermore always accompanied by disappearance of simple cleavage products. The majority of these processes take place exothermically just like the reactions of polymerisation. Such reactive, functional groups are for ex. hydrogen, sulphur or halogen atoms, or hydroxyl, carbonyl, or amino groups. It is to be assumed that no direct conversion occurs primarily between these groups, but that after stimulation of the individual components by warmth or **catalysts** more or less **unstable** intermediate products are formed in primary reactions by addition of components and that not until after their rearrangement and disintegration by cleavage of **molecular** parts and the liberation of heat of reaction, **do stable** final products **arise.** Even a simple ester-formation between two low molecular components permits the assumption of such intermediate forms, as its opposite, the hydrolysis of esters, does not take place directly. Such unstable intermediate products are manifested much more clearly when there is a question of taking hydrogen atoms away from a carbon atom. With phenol and formaldehyde this conversion in an alkaline reaction leads intermediately to the formation of very unstable intermediate products of acetal-like structure, which change immediately to less unstable and therefore tangible oxyphenol alcohols. From urea and formaldehyde arises methylol-urea. Not until after the formation of such primary forms, that is additive compounds with strongly reactive groups, does real polycondensation begin. The exothermic disintegration of these inter-

mediate products furnishes the activating energy for new primary reactions, and the steady change of these processes leads to ever increasing linking of molecules and is controlled by reaction kinetics by the tempo of the origin and of the separation of molecular cleavage products. These low molecular portions of substances require at any rate a superimposition and buffing of the principal reaction and are therefore responsible for a suspension of a definite equilibrium of condensation. Indeed the most diverse means are employed in order to increase the formation of resin in this respect. Thus these reactions represent to a certain extent the **continuation of the processes of condensation,** which themselves lead only to low molecular compounds. Beginning with small molecules, ever higher molecular structures arise, since continually new molecules appear which by their reactive final groups are capable of further conversions, just as far as ring-formation or inner saturation does not occur. Fundamentally these processes can be repeated as often as desired, which would lead to extremely high molecular products. With the growth of the molecules themselves, however, the number of reactive positions in the unit of volume decreases, and the exothermic reactions of polycondensation are more and more slowed up or stopped. Thus the reaction increasing apparently ad infinitum gradually comes to a standstill after mixed substances have gradually formed in this way **threadlike, or ring-formed, or spherical three-dimensional** macromolecules of changing average molecular weight. The well-known resin formation is to be traced back to these processes. According to the previous investigations, successfully conducted by **Carothers,** polycondensation reactions produce **threadlike** macromolecules of an average molecular weight up to 30000[9]). Therewith this reactive possibility of building high molecular substances of thread-like structure is far behind polymerisation since, as is known through **Staudinger,** high polymeric thread-like compounds have been produced and demonstrated up to a molecular weight of 800000. The reason for these differences lies in the difference between the reactions.
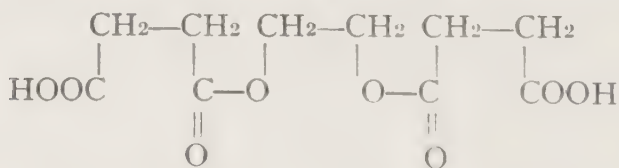
In the **polycondensation reactions** leading to the formation of **three-dimensional** molecules, macromolecules of a considerably greater kind can arise to be sure[10]). Methods for determining the molecular weight of such molecules have thus far not been known, as these products are always insoluble.

According to the number of the reactive positions or

groups in a molecule ("ability to function") and their reactive ability, the course of the processes of polycondensation is directed. If, for ex., ethyl alcohol is converted to ester with acetic acid, the only reactive component of acetic acid is the hydrogen atom of the carboxyl group; in alcohol it is the hydroxyl group. The functionality of each compound is therefore 1, and a reaction 1:1 takes place. On the other hand the prospects of reaction between polyvalent alcohols and polybasic acids or between compounds of the type

$$OH—R—COOH \quad (oxyacids)$$

are much greater, because each of these basic molecules possesses two reactive groups, that is each has the functionality 2. Thus the reaction is $2:2^{11}$). The conversion of glycol and succinic acid in a molecular relationship leads to neutralisation or to the formation of ethylene succinate, that is a diester, which possesses no further reactivity, since there are no reactive groups present in it. In oxyacids, besides **polycondensation,** simple condensations can also take place leading to the formation of low molecular compounds (formation of lactone). Also with changing molar relations arise possibilities leading to the formation of unsymmetrical compounds, as to the formation of half-esters, from which then by excess of one or other components intermediate compounds arise always possessing reactive groups at their ends:

$$\begin{array}{cccc} CH_2—CH_2 & CH_2—CH_2 & CH_2—CH_2 \\ | \quad\quad | & | \quad\quad | & | \quad\quad | \\ HOOC \quad C—O & O—C \quad\quad COOH \\ \| & \| \\ O & O \end{array}$$

These intermediate compounds yield by further condensation with other reactive parts ever larger molecules, which have chiefly an inclination to chain-structure and whose mixtures are highly viscous oils or fusible, thermoplastic, soluble products.

By augmenting the reactive groups on the basic molecules, for example by the use of phenol or of glycerin, both of which possess more reactive positions, the possibilities of conversion are supplemented. Such 3:3- or 3:2- or 3:1- reactions are especially valuable, as such conversions can lead not only to the formation of chainforming high molecular compounds, but also to the genesis of three-dimensional ones, such as result, for

example, in the conversion of phenol with formaldehyde, when the ratio of the gramme molecule of formaldehyde used to the gramme molecules of phenol is greater than 1:1, or when glycerin is converted with polybasic acids.

By the **incomplete saturation** of reactive positions of **medium molecular intermediate products** these substances can be further converted with new primary components, but neighboring chain molecules can also be added later in reticulation, above all when a third reactive position is present, as in phenol[11a]). Such total conversions continued till the cessation of reactivity are the cause for heat hardening, infusibility, insolubility, and lead to disappearance of thermo-plasticity. These relations will be further treated hereafter.

Intermediate Steps of Polycondensation

Although condensation reactions often proceed in lively fashion after excitation, if it is not moderated by suitable control of temperature, the explanation does not need the assumption of the intermediary appearance of radicals as in the case of polymerisation processes, but actually tangible intermediate grades of different average molecular weights are obtained. The course of these reactions is usually longer than that of polymerisation. Such intermediate products are for example resols and novolaks or soluble urea-formaldehyde condensation products. Such substances are of great technological importance and are sought in manufacture also since they possess further convertibility. The control of reactive rapidity and with it the interception of these intermediate products in condensation is after all easily possible, as in condensation reactions low molecular fugitive components are separated which use the heat of reaction for vaporization and thus act as buffers. In polymerisation such intermediate products can not be intercepted as those processes take place so quickly and probably in bulk, but not in degree of polymerisation, are essentially dependent on the time of the reaction. Therefore very high molecular products can be formed in a very short time by polymerisation[12]).

Rapidity of Condensation

Just like the **capacity for condensation,** so the **rapidity of condensation** is essentially determined by the structure of the basic molecule. It is here possible by outer

influences both to slow up or even to stop the reaction, as well as to start or further or continue it, for example if it is not itself capable of activating new molecular components. With many such compounds **already possessing reactive groups,** simple heating is sufficient to induce condensation (for ex. conversion between polybasic acids and polyvalent alcohols). Such substances can be heated alone, for example, or in a mixture, or the condensation can be undertaken by heating in suitable solutions. In many cases the acceleration of such an **autocondensation** takes place by lighting without material additions, although generally such influences are far more effective in polymerisation processes. For example, in the case of vinyl compounds, polymerisations begin very often through the influence of light.

In distinguishing between polycondensation and polymerisation, we must also mention here, principally with regard to the formation of chain molecules, that the rapidity of the polycondensation reaction through **thermic** influences can in no way keep pace with that of polymerisation. Only in comparatively few cases does polycondensation lead to very high degrees of condensation by heating alone, while in the processes of polymerisation these cases occur very frequently. Polymerisates due to warmth and emulsion are, however, very particularly high polymeres while polymerisation by the aid of catalytic agents usually produces only hemicolloids, that is, products of a molecular weight up to ca. 10000[13].

Application of Media of Condensation

High polymeric products occur also under favorable conditions by polycondensation, if condensation media are also added for a more rapid and complete execution of polycondensation processes (obtaining technically useful products) without the application of warmth. These solid, fluid, or gaseous additional substances or expedients are generally of an inorganic nature and it is unnecessary to cite them here in detail. Strong inorganic acids and alkalis are, however, the most effective and most usual condensation media. They are reaction intermediaries and **hasteners,** and even if frequently they have no specific effect, still general applicable regularities prevail. The majority work by means of **homogeneous catalysis,** they form with the reacting substances a physically and chemically uniform mixture and very

often display great effectiveness in extremely small quantity. In individual cases the quantity of the condensation **media** required can, to be sure, be quite considerable, especially when they are consumed in the course of the reaction, by secondary processes, when they are united; for example, by cleavage products. As customary, the **quantities** of condensation media determine here in the homogeneous system also the rapidity of the reactions and very often even small changes of quantity can lead to very diverse and surprising products. In conversions in which the condensation media do not mix with the reacting substances, the current view-points for **heterogeneous catalysis** are no doubt applicable.

To all condensation media then must first of all be ascribed a certain regulation and orientation of the basic molecules, by means of which the formation of unstable intermediate products is mediated and the reactive positions brought closer together. An appropriate choice and application of condensation media is therefore of similar decisive significance for polycondensation processes as for the preparative organic low molecular chemistry. By very slight additions of condensation media to many compounds very active reactions begin even at very low temperatures, while the same compounds are converted solely by heating to a comparatively high temperature only slowly, incompletely or not at all (for ex. phenol and aldehyde).

Procedure in Conversion

By the kind of components or the ratios of their mixture, by the most diverse kinds and quantities of condensation media, and not least by the degrees of warmth—all of them conditions easily controllable in industrial conduct of such processes—possibilities are then present of so regulating the reactions that they can lead to products of diverse composition and diverse high molecular conditions. To this is added the fact that such conversions are undertaken in the presence of diverse solvents and thereby induce further changes. In the synthesis of low molecular compounds by means of condensation very different arrangements and rapidities of reaction can be obtained according to the influence of a solvent. Thus the kind and concentration of such solvents, as well as other influences, as for example the continuous addition of monomeric reaction components to the reaction mixture or the continual addition of condensation

media during the reaction, very strongly determine the whole idea of the reaction, the rapidity of the reaction and not least the properties of the products so obtained. By such measures it is however otherwise possible to control conversions which would otherwise proceed very actively and rapidly; for the reaction proceeds more slowly, the thinner the solution and the lower the boiling point of the solvent. But it takes place also all the more slowly the fewer condensation media there are present. But a slow course of reaction leads according to experience to higher molecular products.

By the knowledge of many such details technology is today in the position of controlling even difficult reactions and of producing uniformly substances of complicated structure. This is for the application, especially of synthetic substances of decisive significance, for industry in continuing its work must expect always to obtain raw materials of constant constitution. Nevertheless unlike products often result in spite of all efforts, knowledge, and elaborated apparatus.

Use of Products of Polycondensation

In many cases the isolation of polycondensation products is very simple, since the high molecular parts are less soluble and fugitive than their raw products. Very often such parts separate even during the reaction or after cooling or precipitation in solid form and can be obtained very easily immediately by filtration. In other cases highly viscous oils separate from the fluid phase which are also easily separated and can be further worked up with corresponding treatment. Usually low molecular dissociation products such as water are constantly removed during the condensation while the reaction is allowed to proceed at a temperature above the boiling point of water. In other cases gaseous and hence easily removable dissociation products occur. In all these reactions the condensates arising are generally used as manufactured products. In the heat there are often oils or viscous resin meltings (condensation products from polybasic acids and polyvalent alcohols, novolaks, resols) or solid insoluble substances (resits). In other cases raw substances remaining unchanged in the reaction (for ex. phenol in the preparation of novolak) are distilled off by ordinary or decreased pressure or by steam. Occasionally such condensation products present in solution with any mixture of substances or other can also

be separated by coagulation, or the solvent is removed by distillation at ordinary or decreased pressure and thus are obtained viscous products which can be further purified and worked up. Often the separation of condensation products and obtaining them in pure condition is renounced and instead the fluid compounds are converted in the heat by addition of solvents into solutions that are used as lacs. This method of work is often the only possible one for further working up condensation products, since highly condensed and therefore hard substances at ordinary temperature are often dissolved with exceeding difficulty and offer difficulties to manufacture in such form.

The non-fugitive codensation media used for condensation remain mostly in the still fusible or even in the non-fusible condensation products and in a given case by liberation of further condensation convert these substances into the final state. In many cases, however, it is necessary to make the condensation media harmless after their use. This can happen, for example, by their transformation into insoluble salts which remain in the products or they can be removed by precipitation or extraction. By the removal of the substances furthering the reaction or their transformation into ineffective compounds, the polycondensation reaction can be slowed up or even stopped, and this measure increases meantime the stability of the final products. By catalyses in heterogeneous systems condensation media are ordinarily removed more easily.

Determination of the Degree of Condensation

Condensation products in fluid phase are usually produced intermittently in uniform charges. But continuous process are also known, for example, mixtures of phenol and formaldehyde together with condensation media or novolaks with hexamethylenetetramine are passed over hot cylinders for a long time until the desired degree of condensation is obtained by dissipation of water or ammonia. In this method of production the partners of the reaction can meet in uniform manner and in equal concentration, and thus the possibility is given sooner for the formation of products of utmost equal average molecular weight and thus of uniform constancy. Nevertheless in technology because of the easier supervision and working, the simpler appartus, the additional possibilities of mixture and other advantages, the intermittent method of work is preferred. It

is a question, however, of polycondensation processes, of separating hydrogen or other gaseous products, then to be sure the continuous method is preferred and the work is done with heterogenous catalysis (condensation of hydrocarbons[14]).

Since high and low molecular compounds are fundamentally distinguished by their physical properties, it is not always easy to characterize high molecular products in ways usual in the case of low molecular substances and to determine corresponding data. A low molecular substance can be obtained by chemical changes as a pure and uniform compound, so that all molecules have the same structure and the same size, while in high molecular substances there are generally mixtures present of varying large molecules[15]). Serving to determine the size of the macromolecule, that is, chiefly the degree of condensation, are viscosity measurements, also determination of solubility and comparisons of solubility in various solvents, melting intervals, properties of flow and determinations of solidity and the like. We have spoken of these already in connection with polymerisation products for which similar view-points are valid.

Properties and Stability of the Products of Polycondensation

The disintegration or **decondensation** of high molecular condensation products by chemical intervention or by the influence of heat on low molecular parts or raw compounds is, in the same way as other chemical and physical properties, considerably dependent on the constitution of the monomeric parts. Moreover there exists here a very essential dependence on the atom groups by which the single molecules are united.

As illustration, esters, as is known, are decomposed by the action of alkali into their original components, that is alcohol and acid. This appears also to a certain degree in products of polycondensation constructed on an ester basis, for ex. the glyptals. In general other grouping of atoms behave in similar manner in the presence of **chemical influences,** while ordinarily the carbon-carbon-union under similar conditions shows a greater firmness and lends remarkable chemical stability to the high moleculars constructed by it. If low molecular compounds which build up the high moleculars, possess relationship to any chemical substance, this relationship is then also present in the larger complexes, but in

lesser degree, since the reactivity of definite groups decreases with the size of the molecule.

Structure of Polycondensates

Of greater significance for chemical stability along with the composition and the size of the molecule is the structure of such polycondensates. Here it is shown that the compounds with thread-shaped or ring-formed structure, usually soft and fusible products, are soluble with comparative ease and more easily accessible to chemical decomposition, while the reticulated or surface-forming structures representing the harder and more viscous substances, show slighter solubility and greater chemical stability. If the high molecular polycondensates are constructed in spherical or three-dimensional forms, they are usually hard and non-fusible, and resist chemical action and usual solvents even when very good solubility must be attributed to the low molecular components. These three-dimensional molecules are also simultaneously most resistant towards thermic influences. On the other hand thread-shaped compounds have a decided inclination by means of thermic or physical influences to disintegrate into low molecular parts as they do under chemical influences. But such a scission in the case of the polycondensates scarcely leads back to the original materials; rather in cracking there often arise new aliphatic or aromatic saturated or non-saturated compounds, according to the constitution of the disintegrating substance and the kind of decomposing influences. If such macromolecular compounds come about by the aid of carbon-carbon-unions, **this** decomposition takes place more easily than with other atom-groupings, and all the more easily, the longer the formation of the carbon chain. Such relations prevail in the case of the polymerisation products, since they have come about generally by union of carbon atoms. A chemically stable and insoluble compound does not necessarily have to be high molecular.

Capacity for Hardening

In the field of high molecular compounds a noteworthy manifestation is the fact that certain compounds apparently of the same composition behave very differently with regard to the influence of warmth and reactivity. For example, one substance is unchanged by heat up to certain limits, it can be fused repeatedly, but another is changed by the influence of heat. Similar

differences are found with regard to solubility and swelling capacity[17]).

The conversion of soluble and fusible initial or intermediate products into a hard, insoluble, and non-fusible state is technically very important and plays a great part in the production of objects of phenoplast or aminoplast as well as in paint materials. Here, especially, such substances are used as are changed during the shortest time possible. They usually originate from polycondensation processes. These compounds capable of hardening are distinguished from the thermo-plastic compounds which are formed according to similar principles of manufacture, especially by the fact that they are changed chemically and therefore change solubility, fusibility, hardness, etc., while these properties remain unchanged in the thermoplastic compounds.
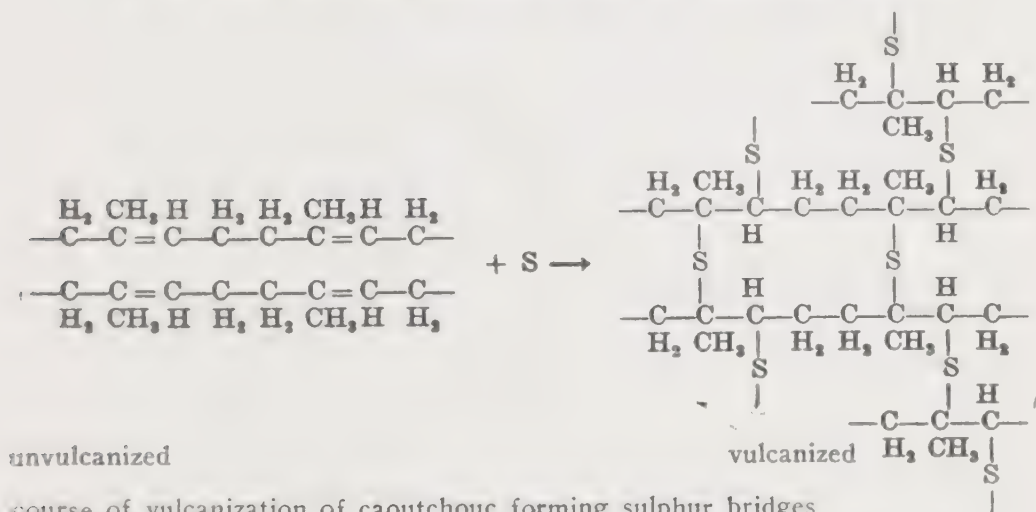
Formation of Three-Dimensional Macromoleculars

Chemically considered, **hardening rests principally on an increase in the size of the molecule,** and especially on the **formation of three-dimensional macromolecules.** Various ways of obtaining such conditions are known:

1. Predominantly hardening is effected by **processes of polycondensation.** Thus in well-known ways by heat or by heat and catalysts, when low molecular compounds are changed, of which at least one has more than two reactive groups, as in the reaction of a gramme molecule of phenol with more than one gramme molecule of formaldehyde. Under certain conditions the formation of the molecule is here completed very rapidly in three dimensions. Hardening occurs when chain-formed initial or intermediate condensation products, such as resols, are further converted while uniting mutually by further condensation of their easily reactive groups by way of definite atom-groupings, solely, indeed, under the influence of heat (formation of resit from resol or resitol by treatment with warmth). From similar raw products, like novolaks, a similar union of molecules takes place with new compounds capable of condensation, when easily reactive hydrogen atoms in para-position are present, to be sure, only when along with the action of warmth condensation media are simultaneously present (formation of resit from novolak with formaldehyde and condensation media, usually hexamethylenetetramine[18]). In both cases the hardening rests on the same causes, principally on the mutual complete saturation of reactive molecules. The relations shown here in one exam-

ple are similarly valid for other resins capable of hardening also.

2. The hardening or the formation of hard and insoluble compounds is also possible by means of **polymerisation processes,** as soon as molecules with more than two reactive positions can be converted or at-

$$
\begin{array}{l}
\text{H}_2\ \text{CH}_3\ \text{H}\ \ \text{H}_3\ \text{H}_2\ \text{CH}_3\text{H}\ \text{H}_2 \\
-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}- \\[4pt]
-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}- \\
\text{H}_2\ \text{CH}_3\ \text{H}\ \ \text{H}_2\ \text{H}_2\ \text{CH}_3\text{H}\ \text{H}_2
\end{array}
\quad + \text{S} \longrightarrow
$$

unvulcanized

course of vulcanization of caoutchouc forming sulphur bridges

vulcanized

tention has been paid to the union of chain-formed macromolecules. Only isolated cases are known in which three-dimensional compounds are formed by simple polymerisation, thus suitable acetylene polymerisation leads to the formation of cuprene. **Staudinger** first showed experimentally in various polymerisation products from styrol and divinylbenzol or only from divinylbenzol, that actually three-dimensional macromolecules occur, which are to be made responsible for insolubility and hardness[19]). But in the great majority of cases polymerisation processes do not lead to polymeric substances capable of hardening, as the requirements for hardening are not usually present here.

3. The **processes of addition that join the molecules** show further possibility for hardening. Hereby are also developed three-dimensional compounds by reticulation from chain molecules already represented. To be sure it is presupposed that the raw materials have non-saturated groups which may be saturated by bivalent atoms or remainders of molecules like sulphur, oxygen, and the like. With the number of such **non-saturated double bonds,** generally present as carbon- carbon-bonds, the possibility of forming such sulphur or oxygen bridges

increases. By this the solubility again decreases and
the hardness of the accruing product is increased. Poly-
merisation products with such non-saturated groups are
especially capable of hardening of this kind, while poly-
condensation products, because of the lack of such non-
saturated positions, are more rarely capable of additive
combination. Especially accessible to this reaction are
caoutchouc, also many polymeric butadien,— vinyl-, or
acetyl- compounds as well as natural drying oils and
the like. The course of vulcanisation of caoutchouc by
sulphur is represented in the adjacent schema as a for-
mation of sulphur bridges to non-saturated molecule
positions[20]).

It is often assumed that intermediate products of
condensation can be hardened only if during the con-
densation non-saturated groups arise giving rise to poly-
merisation and so be said to contribute to an additional
strengthening of the organic substance. In general this
assumption could not prove correct and has scarcely
been demonstrated in any case. On the other hand it can
be demonstrated in the majority of cases which show
continuing condensation with the hardening.

Decisive for the economy of the manufacture of sub-
stances capable of hardening is their **rapidity of harden-
ing**. Lastly it rests also principally on the properties of
the low molecular compounds but can be increased ac-
cording to the conditions by heat and condensation
media.

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ON THE COGNIZANCE OF SOLUBILITY OF HIGH MOLECULAR FILM-FORMING SUBSTANCES

First of all a distinction must be made between three kinds of structure of lacs or paint media:

1. The film-forming part is contained in lac in a comparatively low molecular state and only after charging by oxydation, polymerisation, or condensation, that is by chemical processes, is it converted into a high molecular state. Simultaneously with this increase of the molecule the real paint film appears. To this group of lacs or paint media belong among others drying oils alone, oil lacs from drying oils and natural resins or their products of conversion or synthetic resins of most diverse kind, modified drying synthetic resin lacs, alkyd resin lacs, also lacs capable of hardening by warmth or by the influence of catalysts[1]).

2. The film-forming substance is already found in the production of lac in a high molecular state and it is only by suitable solvents brought to a workable solution, from which it is gradually separated as a film. This process rests solely on physical processes, since no chemical reactions and no size-increases of the molecule take place. Of this description are the lacs on the basis of high molecular cellulose and caoutchouc derivatives and especially also of new synthetic polymerisates[2]) and polycondensates[3]).

3. A low or high molecular compound insoluble in water can under circumstances be converted alone, but mostly by the aid of emulsive media into a drop-shaped distribution form. Such mixtures are then worked up according to the technology of lacs. After charging, there is formed in them by separation of the emulsion and by vaporization of the liquefacient, that is by gradual change of state of the emulsified parts, coherent films whereby in a given case additional chemical processes are not excluded.

New substances ordinarily bring with them new difficulties and for the most part demand a new method of work. The lac industry can often equalize the difficulties present in the individual substance in purely empiric manner by employing the endless plurality of combination possibilities. It is a way that can indeed lead to the goal, but in spite of that can not be regarded as ideal,

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since there always remains a great uncertainty, often finding expression when but slight changes are undertaken.

A certain amount of empiricism can scarcely be relinquished in the production of lac. Meanwhile it will be of great advantage to occupy ourselves with the chemistry of synthetic substances and especially with the basic scientific facts of high molecular chemistry. This new branch of knowledge has been opened up in the last decade by critically scientific researches; at the same time it has been extended technically by German and foreign industry. The result of these efforts is the creation of numerous new lac resins[4]).

THE SOLUBILITY OF
HIGH MOLECULAR COMPOUNDS

In introducing these mostly high molecular lac materials by mere vaporization of the solvents leading to paint films, it was shown at the beginning that their working over to lacs must be conducted from a quite different view-point, than what is valid for the tried and long known oil lacs. The question that has become of especial importance, is that regarding the properties and solubility of the individual high molecular compounds. Knowledge of this is especially important when it is a matter of preparing from synthetic substances with especially favorable properties, for ex. great hardness and resistance, also good usable lacs. These relations are to be treated in the following in order to bring closer to practice the ideas gained regarding the solution of high molecular compounds.

The most conspicuous property of high molecular substances is the high viscosity of their solutions which in many products even in the case of solutions of low percentage can attain extraordinary rates. While previous oil lacs normally have a dry content of about 60% therefore in high molecular raw materials of lac there must have been a transition to diluted solutions, by which the loss of solvent can under circumstances become very great. The industry of synthetic substances also strives to produce raw materials of lac in which in spite of their high molecular weights a comparatively ample solubility is ensured. At the same time the attempt is made to form products that will be compatible with lac benzines, since for well-known reasons they remain the preferred lac solvents.

In high molecular compounds the forces holding them

together between like molecules of the solid substance
are annulled during the process of solution by conver-
sion into a sol. The individual molecules which formerly
were present coherent in the solid substance are mean-
time only normally dissolved and distributed free of
disturbance if sufficient solvent is present. If the solu-
tions evaporate, the dissolved substances will be re-
covered unchanged.

The solubility of the macromolecules is otherwise
determined decisively by their average size or for chain-
formed high molecular compounds by their length. The
higher the molecular weights the more slowly, rarely
and with more difficulty do the compounds in question
dissolve, that is, the general solubility decreases with in-
creasing size or length of the molecules. Further, the
process of solution in the high molecular compounds
because of their structure even in the best solvent is by
no means instantaneous, but is manifested first almost
without exception in strong manifestations of swelling.

Of decisive significance for solubility is the molecular
structure of high molecular compounds, for solubility
depends on that more than on the size of the molecule.
Compounds of different structure, but of equal weight,
can show very considerable differences in solubility. It
is known in general that an irregular unsymmetrical
structure or a branching of the chain structure contri-
butes considerably to increasing the solubility, while at
the same time the melting point of such substances is
lowered. Thus methyl-or other side groups in high mole-
cular carbon chains further solution greatly. This is
shown very instructively by a comparison of solubility
of comparatively low molecular paraffin hydrocarbons
with normal chains on one side and branched chains on
the other. Thus high molecular paraffins with a normal
chain are dissolved, for ex. buna, with comparative dif-
ficulty, while natural caoutchouc, but still more so
methyl- or ethylhydrocaoutchouc are soluble with com-
parative ease. From similar reasons modified phenol-,
cresol-, and alkylphenolresins show better solubility and
compatibility with drying oils than pure phenolresins.
High molecular compounds of chainformed structure,
such as for ex. cellulose ester, polystyrol, polyvinylace-
tate, polyvinylchloride, polyvinylether, polyacrylates and
the like, are more easily soluble than products of reticu-
lated or spherical form, as present in resitols, in definite
alkyd resins, or even in resits. Compounds of reticulated
structure also show, if they are sufficiently high mole-

cular, usually extraordinarily strong transient or per-
manent manifestations of swelling the majority of which
lead to a manifold increase of volume and form gels.
Their solidity is again a function of their molecular size
and often can not be influenced by further adidtions of
solvent. Lacs in which there are such manifestations,
proceed badly, show a lack of film-lustre and unsatis-
factory drying capacity; they can be improved in many
cases only by suitable solvents or solution mediators.

High molecular lac raw materials often possess from
the reasons given a very great stability in the presence
of solvents, and are therefore often soluble only in very
definite solvents. Therefore it is often compulsory to
turn to dear special solvents or to use complicated sol-
vent mixtures in order to attain ample solubility in con-
nection with regular re-evaporation and uniform film-
formation. The paint films obtained then show again a
very considerable solvent stability indeed, which is
slight only in the presence of special solvents.

Meantime the **influence of definite groups in** high
molecular compounds and solvents makes itself decided-
ly noticeable in connection with the solubility. Although
a definite law can not be formulated, yet definite re-
lations between solvents and the substances to be dis-
solved can be determined. This is indeed especially true
for low molecular compounds. For in high molecular
products the influence of individual groups can appear
only rather weak, especially if they form but a slight
percentage in a larger basic molecule. Even in the homo-
logous series of low molecular alcohols and acids, also
of the aldehydes and ketones, solubility decreases for
ex. in water, the more the oxygen content of these com-
pounds recedes in relation to the carbon content, while
the solubility of the higher homologues in hydrocarbons
increases correspondingly. Fundamentally an improve-
ment in solubility of compounds with hydroxyl-, amino-,
ether-, ester-, halogen-, and alcohol-groups is decidedly
noticeable in solvents bearing similar groups. Actually
the majority of the usual high molecular lac raw ma-
terials possess such functional groups.

The influence of the relation of the solvent to a high
molecular compound is especially manifested in the fact
that very many of these substances are not very easily
dissolved in their monomeric raw product, although there
is here no lack of exceptions. Thus polystyrol is dissolved
in monomeric styrol or a high molecular phenol-for-
maldehyde- resin product in phenol or cresol, when other

solvents have long failed. The more a high molecular
compound is furnished with such influential groups, the
greater is their solubility. By the entrance of alykyl-
groups in compounds containing oxygen, solubility be-
gins in hydrocarbons while at the same time they are
diminished in solvents containing oxygen. Besides high
molecular hydrocarbons like caoutchouc, buna, polyiso-
butylene or polystyrol, also butadien-, isoprene-, or vinyl
derivatives such as chlorcaoutchouc, polychlorbutadien
(duprene), polyvinylchloride and the like are soluble
with difficulty in solvents containing hydroxyl or oxy-
gen, or even insoluble, as long as otherwise they bear no
groups containing oxygen, but on the other hand, in cor-
respondence with their molecular weight, they are very
considerably soluble in hydrocarbons or their halogen
compounds. But high molecular compounds containing
oxygen, like cellulose, cellulose ester and cellulose ether,
starch, polyvinylalcohol (polyviolan), polyvinylacetate
(vinnapas, mowilith), novolak, resol (lac raw material
resinol LIV), alkyds (alkydal, glyptal), polyacrylate
(plexigum) are insoluble in hydrocarbons. In some of
these compounds the influence of the carbon towards or-
ganic solvents is repressed by the great number of their
hydroxyl groups, and mediates solubility in water. Such
compounds are then soluble with difficulty or not at all
in alcohols, ketones and others, although compounds
with oxygen content incline to solution in alcohols, es-
ters, ketones, ethers, acetates, acids and the like. If
definite groups form salts easily, the latter mediate
solubility of the high molecular compounds in alkalis.
organic bases, or acids and in this way form high mole-
cular soluble salts. In this way are dissolved without dif-
ficulty novolaks and resols, condensates of urea and
anilin, polyacrylic acids each after its fashion in alkalis
or acids and in these solvents also lead in a given case
to highly viscous solutions.

Compounds with strong polaric hydroxyl anine or
carboxyl groups, as they are present in polyhydroxyl,
polyamino compounds, and polycarboxylic acids, can how-
ever, in greater concentration in solvents having the same
groups, that is in water or alcohol. by association, aggre-
gation, formation of micelles and clusters lead to manifes-
tations which simulate a considerable genuine increase in
size of the molecule (as it is known for ex. in polymerisa-
tion or polycondensation processes) and give to their so-
lutions far too great a viscosity according to the con-
stituence of the dissolved substances, a viscosity exceed-

ing the increase to be expected. Here it is a question of false increases of the molecule occurring through the assemblage of polar groups or through the retention of the solvent in the substance to be dissolved. Such relations are especially favored in concentrated solutions and at temperatures approximately below 50° C, while genuine solutions are almost always present in very dilute solutions. At a higher temperature such association colloids are unstable; they decompose as can be noted outwardly by the decrease in viscosity of their solutions. The decrease in viscosity is stronger in proportion as it corresponds to a decrease in viscosity of normal solutions by heat.

In the majority of cases later increased dilution with good solvents leads to normal states of solution. since disaggregation sets in, that is the colloid particles are separated. Furthermore additions of electrolytes or of compounds with strong polar groups, not identical with these of the substance to be dissolved, also small quantities of non-solvents, effect a return to normal conditions of solubility. Therefore on this account as well as for other reasons mixtures of solvents are preferred in the lac industry. In all these processes however the momentary conditions of solution vary again and again greatly, dependent on the molecular weight of the high molecular compounds.

For many high molecular substances the relations named, leading to the formation of a new molecule bond, are decisive in attaining solubility. This is recognized for ex. in the alkylethers of cellulose, especially in methylcellulose. Such substances are today used as emulgents, adhesives, and binding agents under various trade names. Methylcellulose is soluble in cold water but insoluble in hot. By heating cold methylcellulose solutions the solid substance is again formed and separated unchanged. According to investigations by **Staudinger** methylcellulose with cold water first forms an intermediate compound which is dissolved by still more cold water and only then is a solution made possible, since a cellulose ether must really be insoluble in water because of its constitution. This intermediate compound is not stable under heat and disintegrates[5]). On the other hand cellulose ethers such as for ex. the benzylcellulose used in the lac industry are soluble in various organic solvents such as butylacetate because of their relationship to the solvent. Such intermediate compounds that facilitate solution are in many cases to be held re-

sponsible for good solution in the preparation of lac and the production of synthetic resins.

SOLUTIONS OF PAINT MEDIA

The ideas previously put forward can in many cases serve without addition as explanation of estimations established in numerous scientific investigations of lac and paint media and published, for which however a consistent interpretation does not exist. But it is not surprising that many conclusions are contradictory, if we consider that such investigations can only be carried out in systems in which many components share simultaneously. Further, for ex., relations determined at 20° C. can not be directly transferred to higher temperatures.

Thus there are found frequently in literature statements about the different behaviour of lac raw substances in the presence of solvents in various degrees of concentration, and also of their capacity for forming film[6]). Further it is known to practice and has been demonstrated by investigations that after addition of definite solvents[7]), softeners[8]), resins and even water to lac solutions their viscosity is either increased or diminished. If, for ex., caoutchouc solutions are treated with oxydation media, tin tetrachloride or p- sulphotoluenic acid, there is a decrease of viscosity. Such methods are often recommended for assuring smearing capacity of lacs, but are unprofitable, since the decrease of viscosity occurs at the expense of firmness of the film, hardness and capacity for resistance.

In cases, in which for ex. by additions of butanol to ester solutions of high molecular wools there are increases of viscosity far exceeding that to be expected on the basis of the higher proper viscosity of butanol, or where by additions of toluol, benzine or carbon tetrachloride to similar solution in definite fields and in the case of various types of wool there also appear increases of viscosity, these manifestations are due to causes not to be explained by the foregoing statements. If increases or decreases of viscosity appear by additions of softening media or resins, these manifestations are also comprehensible. If, for ex., nitrocellulose, which as is known does not correspond to trinitrating cellulose and therefore still possesses **free** hydroxyl groups in its cellulose chains, is dissolved in ester mixtures and replaced by butanol, then new, larger colloid particles appear formed by the association of several nitrocellulose molecules or by the assistance of the solvent; the result is an in-

crease of viscosity. The accumulation of molecules is conditioned by the still free hydroxyl groups of the cellulose chain and of the solvent, otherwise a decrease in the viscosity of the solution would appear because of the improvement of the state of the solution. With increased nitrogen content or with higher molecular weight this influence becomes slighter. In this way the influence of butanol as medium of flow and action, especially in the case of cellulose- and phenol-formaldehyde resin lacs is clear, since by means of butanol the high molecular substance remains longer in the plastic state as shown in lac technology by slower drying, good progress and formation of smooth top surfaces.

The increase of viscosity of wool solutions in butyl-acetate after gradual addition of toluol, benzine, and carbon tetrachloride depends on diminishing the capacity for solvation of the solvents by hydrocarbons. From these reasons, first as a consequence of association an increase of particles or gel formation takes place with especial ease in concentrated solutions, whereby at the same time there is a gradual deterioration of the distributing condition, which finally leads to precipitation whereby the proper viscosity of the solvent is retained.

Here we must further note that the precipitation of a high molecular substance from a solution depends on the molecular weights of the substance dissolved, the concentration of the solution and the kind and quantity of the precipitant. For the precipitation of high molecular compounds a smaller quantity of the precipitant is necessary than for low molecular compounds. In low molecular wools or in non-concentrated solutions therefore such additions cause small or only slight increases of viscosity, for from well-known reasons they dissolve more easily and require less solvent for solution. Cresol-novolaks and cresol-resols dissolved in alcohol-toluol, decrease their viscosity if more toluol is added, because no normal solution is present in the alcohol-toluol-mixture; this only started by the strengthened influence of the methyl groups of the one solvent. Phenol-novolaks and phenol-resols give increase of viscosity with an increasing toluol content, because in this case the hydroxyl groups of the phenol only are noted as decisive. Softeners and resins, finding application in lacs of high molecular substances, are proven mediators of solution both for the substance to be dissolved and especially for additions which can not be combined without their presence, but simultaneously in the majority of cases because of

manifestations of association cause abnormal increases of viscosity which must be taken into account in the application of such substances. The typical behavior of the individual lac materials in solutions depends therefore predominantly on the structure of the molecule.

If successful in undertaking changes in lac raw substances by the introduction of especial groups, then completely new relationships of solubility enter[9]). It could also be determined by acetylization of a cellulose only partly ethylated, that it is only dissolved normally in benzol, while before the acetylization in benzol associated colloid particles were present, for a solution of ethyl cellulose in benzol is reduced by addition of water to portions of the original viscosity value[10]). Here as in the case of the nitrocelluloses the still free hydroxyl groups of the cellulose chain strongly influence the state of solubility. Only when, as the foregoing experiment shows, the influence of the hydroxyl groups is eliminated by acetylization, can such benzol solutions be replaced by water without change of viscosity. Many similar changes of viscosity appearing often in the solution of high molecular substances and especially in the production of lac can be indicated by analogy. Such manifestations often appear unintentionally and cause partially unpleasant disturbances.

SUMMARY

In the foregoing statements an attempt has been made to give in broad outlines a survey of the interesting questions connected with the production of lacs or paint media from high molecular lac raw materials. For the difficulties met in practice in the solution of high molecular compounds, the cause is partly to be seen in the nature of the lac raw materials at disposal. There is however in progress in this field a work on structure which promises to be successful, in which the aim is, along with others, to simplify the manufacture and make it easier. The attempt will also be made by mutual chemical transpositions, especially by introducing definite groups in existing high molecular substances to improve the reactivity and limits of solubility during treatment.

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